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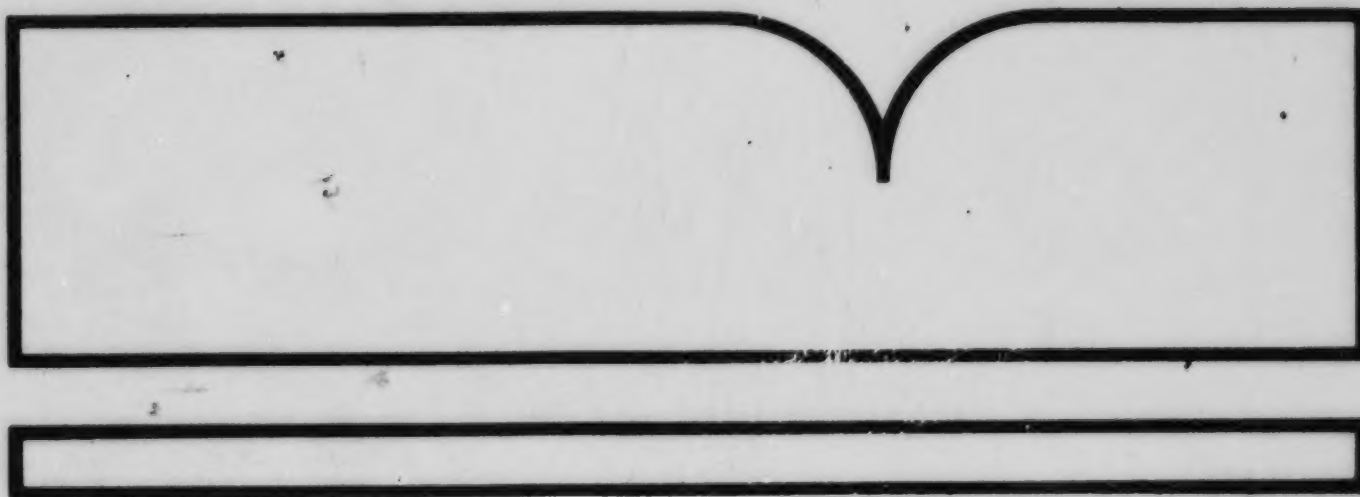
Assessments of Future Environmental Trends and
Problems of Increased Use, Recycling, and
Combustion of Fiber-Reinforced, Plastic and
Metal Composite Materials

Versar, Inc.
Springfield, VA

Prepared for

Environmental Protection Agency
Washington, DC

14 Jul 82



U.S. Department of Commerce
National Technical Information Service

NTIS

PB82-255514

EPA 600/8-82-019
July 1982

ASSESSMENTS OF FUTURE ENVIRONMENTAL TRENDS AND PROBLEMS OF
INCREASED USE, RECYCLING, AND COMBUSTION OF FIBER-REINFORCED,
PLASTIC AND METAL COMPOSITE MATERIALS

Contract No. 68-02-3636

FINAL REPORT

Prepared For:

Office of Strategic Assessments and Special Studies
U.S. Environmental Protection Agency
Washington, D.C. 20460

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JULY 14, 1982

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SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC INFORMATION

PB82-255514

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George Provenzano.

PERFORMER: Versar, Inc., Springfield, VA.
Contract EPA-68-02-3636

SPONSOR: Environmental Protection Agency, Washington, DC.
EPA/600/882/019
Final rept.

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KEYWORDS: *Composite materials, *Environmental impacts.

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PRICE CODE: PC A12/MF A01

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**Mention of trade names or commercial products does not
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SECTION 1

SUMMARY AND CONCLUSIONS

The purpose of this study is to identify and define future environmental concerns related to the projected utilization, recycling, and combustion of composite materials. This study is being conducted for the Office of Strategic Assessment and Special Studies (OSASS) of the U.S. Environmental Protection Agency (EPA). Based on results of this study, EPA will make a preliminary determination of whether further study is warranted for any of the potential environmental concerns that this study identified as being associated with composite materials use and disposal and assign research priorities in this area.

At the outset of this project, it was decided that the materials to be studied would include all varieties of composites and their components (i.e., plastics, metals, and ceramics reinforced with fibers such as glass, graphite, Kevlar®, boron, etc.). Thirty components, both fiber and matrix, were investigated. Based on projected utilization rates to the year 2000, eight of these materials, listed in Tables 1-1 and 1-2, were selected for in-depth environmental assessments. An extensive background and literature search was then conducted to determine what toxic properties, if any, and what potential public health and environmental risks may be associated with these materials or their combustion products. This information was incorporated into chemical monographs, which are included as appendices to this report on each of the eight substances.

TABLE 1-1
PROJECTED ANNUAL PRODUCTION OF MAJOR REINFORCING FIBERS
1980 - 2000**
(Millions of Pounds)

<u>Fiber Type</u>	<u>Year</u>		
	<u>1980</u>	<u>1990</u>	<u>2000</u>
Graphite	2	27.6	71.6
Glass	880	1,200	2,000
Kevlar®	1.2	8	*
Silicon carbide whisker	0.002	1.5	*
Silicon carbide filament	0.0002	0.1	0.26

* Insufficient information to make reasonable estimate.

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** Projections based on analysis contained in Section 4.

TABLE 1-2
PROJECTED ANNUAL PRODUCTION OF MAJOR MATRIX MATERIALS FOR USE IN COMPOSITES
1980 - 2000**
(Billions of Pounds)

<u>Resin Type</u>	<u>Year</u>		
	<u>1980</u>	<u>1990</u>	<u>2000</u>
Polyester	1.1	1.6	2.4
Epoxy	0.065	0.13	0.25
Vinyl ester	0.021	0.030	0.05

** Projections based on analysis in Section 4.

Based on the results of the literature search, the eight materials were assigned to one of four groups with recommended follow-up actions. The criteria for assigning the materials to one of the four groups were: (1) whether the materials have been listed as toxic or hazardous materials under the Clean Air Act, the Clean Water Act, or the Resource Conservation and Recovery Act; or (2) whether they have been identified as hazardous to the environment for health or non-health related reasons by any other documented sources. The four groups are identified as follows:

- Group 1 includes materials or their combustion products which have not been listed as hazardous by EPA or for which no health or nonhealth* hazard has been identified to date; therefore, further investigation can be postponed in favor of materials in high priority groups.
- Group 2 includes materials or their combustion products which have been identified as presenting some potential for non-health related hazards and, therefore, further investigation may be warranted to resolve the uncertainties.
- Group 3 includes materials or their combustion products which have been identified as presenting some potential for health-related hazards and, therefore, further investigation is warranted to resolve the uncertainties. Follow-up actions might involve making a scientifically comprehensive risk assessment and consideration for inclusion in the appropriate EPA list and/or investigation to identify safe combustion practices.
- Group 4 includes materials or their combustion products that have been included on an existing EPA toxic or hazardous substances list.

*The only non-health hazard of concern is the shorting-out of transformers and other electrical equipment caused by the discharge of carbon fibers into the atmosphere as a result of the incineration of graphite fibre reinforced composites.

No material or combustion product was assigned to Group 4. In the area of use, no potential health or non-health hazards were identified; with respect to combustion, four materials were found to generate under certain laboratory conditions combustion products listed as hazardous by the EPA. These materials included: epoxy, polyester, vinyl ester, and Kevlar®. It should be noted that the combustion products data were collected during various types of combustion (i.e., pyrolysis, uncontrolled burning, etc.), which are not typical of proper incineration practices. It is possible that the identified toxic combustion products may not be present under proper incineration conditions, hence, their inclusion in Group 3. Finally, graphite fibers were assigned to Group 2 due to the potential electrical problems associated with their airborne release during incineration.

● Graphite fiber	Use	Group 1
	Combustion	Group 2
● Glass fiber	Use	Group 1
	Combustion	Group 1
● Silicon carbide filament	Use	Group 1
	Combustion	Group 1
● Epoxy resin	Use	Group 1
	Combustion	Group 3
● Polyester resin	Use	Group 1
	Combustion	Group 3
● Vinyl ester resin	Use	Group 1
	Combustion	Group 3
● Kevlar® fiber	Use	Group 1
	Combustion	Group 3

An analysis of the recycling indicated that the most economically and environmentally viable recycling option would be burning for energy output. However, various kinds of fiber make up a major component of the composite materials and complicate the combustion process. Graphite fibers should be contained because atmospheric release could result in electrical problems in the vicinity of the incinerator. Glass fibers will present slag

problems if they are melted in the incinerator. In addition, the previously noted problems associated with improper combustion would have to be addressed.

The primary type of pollution from the use, combustion, and recycling of composite materials is airborne pollutants from the combustion of waste materials. Therefore, any future research efforts in this area would be of particular interest to the EPA's Offices of Solid Waste and Air Quality Planning and Standards.

SECTION 2

INTRODUCTION

PURPOSE OF STUDY

The purpose of this study is to identify and define future environmental concerns related to the projected utilization, recycling, and combustion of composite materials. This study was conducted for the Office of Strategic Assessment and Special Studies (OSASS) of the Environmental Protection Agency. Based on this report, EPA will make a preliminary determination of whether further research is warranted for any of the potential environmental concerns that this study identified as being associated with composite materials use and disposal, and what EPA's research priorities in this area ought to be.

The Office of Strategic Assessment and Special Studies (OSASS), one of two offices in the Office of Research and Development's (ORD) Office of Exploratory Research (OER), is responsible for providing information about future environmental trends and problems to the Assistant Administrator for Research and Development, his Office Directors, and other participants in the EPA's R&D planning and policymaking processes.

OER is responsible for providing "over the horizon" inputs into the R&D planning process both by identifying, defining, and assessing future environmental trends and problems and by conducting exploratory research to satisfy basic information needs concerning future problems. Within OER, OSASS has primary responsibility for the former and shares responsibility for the latter with the Office of Research Grants and Centers. Specifically, OSASS is responsible for producing reports that: (1) provide a reasonably comprehensive, integrated overview of the longer-term regional, national, and global environmental outlook; (2) expand existing data bases and increase understanding of potentially significant future problems; and

(3) evaluate concepts, methods, models, and environmental controls and policies as they affect the environmental future. Collectively, these reports are intended to: (1) produce a description of alternative future trends and contingencies and an analysis of their environmental consequences, including their public health, public welfare and policy implications and (2) identify research that should be conducted to support EPA's regulatory mission in the future.

SCOPE OF PROGRAM

This project assessed the potential environmental impacts of projected utilization, recycling and combustion of composite materials over the time period from 1981 to the year 2000. For the purposes of this study a composite material is defined as a material, commonly called a matrix, such as a plastic, metal or ceramic which is reinforced through the additions of fibers in order to improve its physical properties (i.e., strength, stiffness, etc.).

Versar first assessed the current and projected applicability and usage of the following 30 matrices and fibers:

• Matrices

Plastics

Epoxy
Polyimides
Phenolics
Epoxy/Novolacs
Melamines
Vinyl esters
Polyesters
Polysulfones
Polyphenyl sulfones
Polyamide/imides
Polycarbonate
Polyphenylene sulfide

Metals

Aluminum
Magnesium
Titanium
Superalloys

Ceramics

Carbon
Silicon Nitride
Boron Nitride
Silica

Acrylonitrile Butadiene Styrene (ABS)
Nylon
Polyether sulfones

Glass

- Reinforcing Fibers

Graphite
Aramid (Kevlar®)
Glass
Boron
Boron nitride
Silicon carbide

To this list of materials, Versar applied the methodology that is described in the section that follows.

METHODOLOGY

Versar conducted an extensive background and literature search to:

- (a) Provide information for identifying and analyzing alternative future trends in the use of composite materials.
- (b) Provide information for assessing the potential public health and environmental risks associated with these usage trends.

With respect to the information needed to identify and analyze usage trends for composite materials, the search obtained the following types of data:

- Types of composites in general use.
- Types of composites projected to come into use.
- Industries involved.
- Current users.
- Potential users.
- Present production.
- Projected production.
- Supply and demand (including market prices) factors that affect the rates of composites production and use.

With respect to the information needed to assess potential health risks, the search obtained, where available, the following types of data:

- Results of controlled toxicological studies.
- Clinical observations of accidental exposures.
- Epidemiological data.

With respect to the information needed to assess potential environmental risks, the search obtained, where available, the following types of data:

- Physical, chemical, and biological impacts on air, water, and land.
- Global, regional, and local effects, including the effect of composite materials on indoor air quality.
- Relevant environmental transport data.
- Pertinent EPA regulations.

This first phase of the research also involved a series of visits and contacts with experts in the composite materials field. These visits were organized to include at least one expert from each major segment of the industry: fiber manufacturers, resin or other matrix manufacturers, and manufacturers who use composites. These visits emphasized, but were not limited to, the production and use of composite materials for potential large-scale civilian applications. Three major trips were made.

Trip 1: - Air Force Materials Laboratory; Dayton, Ohio

Trip 2: - Detroit, Michigan

- Chrysler
- Ford
- General Motors

Trip 3: - Union Carbide; Danbury, Connecticut

- Avco; Lowell, Massachusetts
- Army Materials and Mechanics Research Center; Watertown, Massachusetts
- Ciba-Geigy; Ardsley, New York

Numerous contacts in the Washington, D.C., area were made, including the following:

- U.S. Navy
 - Naval Sea Systems Command
 - Naval Surface Weapons Center
- Fort Belvoir
- NASA
- U.S. Department of Energy

Additional telephone contacts also were made with matrix and fibre manufacturers, intermediate manufacturers, and fabricators, such as:

- Boeing Commercial Aircraft Company
- Lockheed - California Corporation
- DWA Composite Specialtics, Inc.
- Fiberite Corporation
- Hexcel Corporation
- U.S. Polymeric, Inc.
- Fiber Sciences, Inc.
- Corning Glass Works, Inc.
- E. I. Du Pont de Nemours, Inc.
- Trade Associations, including the Society of Plastic Industries and Society for the Advancement of Materials and Plastics Engineering

The second phase of this search involved the development of chemical (or material) monographs for composites and their components that were identified in phase one. The elements addressed in a monograph are outlined in Figure 2-1. Monographs were prepared for graphite fiber, Kevlar®, glass fiber, silicon carbide filament and whiskers, polyester, epoxy, and vinyl ester. These monographs are included as appendices to this report.

Primary and Secondary Review of Recent Literature

Chemical(s) definition information was used to construct an initial generalized search of the computerized data bases. The core sources of information are presented in Table 2-1. This list was divided into primary and secondary sources.

- I. CHEMICAL INFORMATION
 - A. Nomenclature
 - 1. Name
 - 2. Chemical name
 - 3. Synonyms
 - 4. Gas registry number
 - 5. Wiswesser line notat.
 - B. Empirical Formula
 - C. Structural Formula
 - D. Molecular Weight
 - E. Specifications
 - 1. Chemical
 - 2. Official compendia
 - F. Description
 - 1. Gen. characteristics
 - 2. Physical properties
 - 3. Stability
 - G. Analytical Methods
 - H. Breakdown
- II. ECONOMIC FACTORS
 - A. Production
 - 1. USA
 - 2. Imported into USA
 - 3. World
 - 4. Natural occurrence
 - 5. Major prod. and dist.
 - 6. Methods and processes
 - 7. Market price
 - B. Consumption
 - 1. Major uses
 - 2. Minor uses
 - 3. Discontinued uses
 - 4. Projected uses
 - 5. Possible alternatives
 - C. Environmental
- III. PERTINENT REGULATIONS
- IV. TOXIC/BIOCHEM. INFO.
 - A. Human Exposure
 - 1. General population
 - 2. Occupational exposure
 - 3. Organ toxicity
 - B. Human Pharmacokinetics
 - C. Animal Toxicity
 - 1. Acute
 - 2. Subacute
 - 3. Chronic
 - 4. Long-term
 - D. Animal Pharmacokinetic
 - 1. Adsorp. and distrib.
 - 2. Metabol. and excret.
 - 3. Enzymatic effects
 - 4. Chemical interactions
 - 5. Organ toxicity
 - 6. Toxicity comparisons

FIGURE 2-1. INFORMATION ELEMENTS FOR MATERIAL MONOGRAPHS

TABLE 2-1
CORE SOURCES FOR LITERATURE REVIEW

<u>Core Journals</u>	<u>Availability*</u>
<u>Primary Sources</u>	
Agricultural and Biological Chemistry	FDA, NAL, NOAA, NLM
Journal of Environmental Science and Health	CPSC, EPA, NLM, NBS, NAL, NOAA
Advances in Comparative Physiology and Biochemistry	NOAA, EPA, NLM, NAL
Analytical Biochemistry	EPA, FDA, NOAA, NBS
Biochemical Pharmacology	CPSC, EPA, FDA, OSHA
Biochemistry	NBS, CPSC, EPA, FDA, NOAA, OSHA
Clinical Biochemistry	NLM, NAL
Journal of Biochemistry	EPA, FDA, OSHA, NBS, NLM, NAL
Environmental Health Perspectives	CPSC, EPA, FDA, OSHA, NOAA, NLM
Environmental Pollution	EPA, NBS, NOAA
Journal of Environmental Health	CPSC, EPA, NLM, FDA, OSHA
Food and Cosmetics Toxicology	EPA, FDA, OSHA, NLM
Mutation Research	EPA, FDA, OSHA, NAL, NLM
American Industrial Hygiene Association Journal	CPSC, EPA, FED, OSHA, NLM
American Journal of Epidemiology	CPSC, NLM, EPA, FDA, NOAA OSHA
Journal of Occupational Medicine	EPA, FDA, NLM
Pharmacology	EPA, FDA, NLM
Cancer	EPA, FDA, NLM
Cancer Research	EPA, FDA, OSHA, NLM
Clinical Chemistry	EPA, FDA, NBS, NLM
Journal of Physical Chemistry	EPA, FDS, NLM, NBS, NOAA
Review of Economics and Statistics	CPSC, EPA, DOI, NBS
Archives of Environmental Contamination and Toxicology	EPA, FDA, NLM, NOAA, NBS

* Descriptions of library acronyms are provided at the end of the table.

TABLE 2-1
(continued)

<u>Core Journals</u>	<u>Availability*</u>
<u>Primary Sources (continued)</u>	
Archives of Environmental Health	CPSC, EPA, FDA, NBS, NLM, DOI
Environmental Science and Technology	EPA, FDA, NOAA, NBS, OSHA
Archives of Industrial Hygiene and Occupational Medicine	EPA, FDA, NLM
Toxicology and Applied Pharmacology	CPSC, EPA, FDA, NOAA, OSHA
Journal of Occupational Medicine	CPSC, EPA, FDA, OSHA, NLM
Science	CPSC, EPA, FDA, DOI, NOAA OSHA, NBS
<u>Secondary Sources</u>	
Agricultural Engineering	
Agricultural Research	
Agricultural and Environment	
Agronomy Journal	
American Journal of Agriculture Economics	
Animal Feed Science and Technology	
Experimental Agriculture	
Journal of Agricultural and Food Chemistry	
Journal of Agricultural Research	
Journal of Pesticide Science	
Pesticide Science	
Annals of Clinical Biochemistry	
Biochemical Journal	
Comparative Biochemistry and Physiology	
International Journal of Biochemistry	

* Descriptions of library acronyms are provided at the end of this table.

TABLE 2-1
(continued)

Core Journals

Secondary Sources (continued)

Journal of Biological Chemistry
Molecular and Cellular Biochemistry
Environmental and Experimental Botany
International Journal of Environmental Studies
International Journal of Occupational Health and Safety
Water Resources Bulletin
Atmospheric Environment
Environmental Research
International Journal of Environmental Analytical Chemistry
Journal of Environmental Sciences
Journal of the Air Pollution Control Association
Journal of the Water Pollution Control Federation
Journal of Agricultural and Food Chemistry
Journal of Food Science
Annals of Human Genetics
Journal of Genetics
Polymer Engineering and Science
Molecular Pharmacology
Life Sciences
International Journal of Cancer
ACS Symposium Series
Journal of the American Chemical Society
Analytical Chemistry
Chemical Physics
Journal of Applied Ecology
Journal of Economic Study
Biology of Reproduction
International Journal of Engineering Science
Journal of Occupational Accidents

TABLE 2-1
(continued)

Core Journals

Secondary Sources (continued)

Pollution Engineering
Chemical Engineering
AIChE Journal
Hydrocarbon Processing
Process Engineering
Bulletin of Environmental Contamination and Toxicology
Environmental and Experimental Botany
Environmental Pollution
Anesthesiology
Industrial Engineering Chemistry
Kirk-Othmer Encyclopedia of Chemical Technology
British Journal of Industrial Medicine
Nature
Journal of Toxicology and Environmental Health and Science

- * CPSC = Consumer Product Safety Commission Library
- EPA = Environmental Protection Agency Library
- DOI = Department of the Interior Library
- FDA = Food and Drug Administration Library
- NOAA = National Oceanic and Atmospheric Administration
- NLM = National Library of Medicine
- OSHA = Occupational Safety and Health Administration
- NBS = National Bureau of Standards Library
- NAL = National Agricultural Library

Every required monograph topic was thoroughly covered with a reasonable degree of redundancy. However, it should not be concluded that the sources listed are complete. Additional sources of information were developed as the studies progressed.

The results of the initial automated search were reviewed for direction, thoroughness, and accuracy. This review was returned to the researchers, and a second search was constructed with additional authors, key words, descriptions, identifiers, and sources that were particularly relevant. Both the program manager and researchers reviewed the results of the second search and assessed the information for relevance.

Manual Review of Recent and Retrospective Information

Because computerized data bases are a relatively recent development and contain little information on research before 1970, literature prior to this date was recovered manually using traditional search techniques. It was recognized that the limitation of automated searching is that parallel or tangential data can be overlooked by computers but picked up by manual review of the literature. The output of the first two steps of research was used to guide the researchers through a review of the literature covering the period from 1920 to the present.

Data Collation and Review

Relevant data were assembled through the full research process. These documents and data were collated by the researchers and used to complete monographs for the various materials that were studied in depth.

Trends Analysis

Based on the information gathered in the literature search, trends in the production, use, and ultimate disposal of composite materials were identified and analyzed. The analysis was conducted for various specified economic, technological, and regulatory scenarios that, in effect, defined a range of future utilization levels for composite materials.

Hazard Analysis

At the outset, it was intended that a quantitative risk analysis would be performed based on an assessment of existing information on the relationship between a material's environmental exposure or its combustion products' potential for toxicity. The lack of quantitative toxicity and exposure data precluded any such a risk analyses from being made. Therefore, only qualitative analyses of the hazard potential for adverse health and ecological impacts could be made. These are in Section 5.

SECTION 3

COMPOSITE MATERIALS: STATE OF THE ART

DEFINITION

A composite material is the mixture of two or more solid materials that results in a material structure with enhanced physical properties. The components of the mixture consist of a matrix such as a plastic resin, metal, or ceramic and one or more materials in the form of fibers embedded in the matrix. These fibers impart improved properties to the matrix such as improved strength, stiffness, and toughness.

HISTORY

Composite materials have existed in nature since the beginning of our time in the form of wood and bone. The conceptual idea of a composite, the combining of materials to produce a single material with improved properties, has been put into practical use by both man and animal since their earliest existence. A number of primitive civilizations found that brick strength was improved by mixing straw into the mud before forming and drying. Barn swallows use the same technology in construction of their nests. The early Egyptians formed improved wood tool parts by gluing thin strips of wood together.

The beginning of modern day composites was marked by the filing of a U.S. patent for a structural glass fiber reinforced plastic in 1916 by Robert Kemp.⁽⁴⁾ The first commercial production of glass fibers by Owens-Corning in the late 1930's began serious development of fiber-reinforced plastics, as addressed by this study. The first applications

for these new plastics were for aircraft components.⁽³⁾ With the advent of radar, fiberglass-reinforced plastics were used in the radoms (antenna covers) of a number of late World War II aircraft. The synthesis and development of epoxy resins in the 1950's provided greatly improved weathering characteristics to fiberglass-reinforced systems, which saw increased application in the Air Force's helicopter programs. The 1960's brought applications for fiberglass-reinforced plastics to aerospace systems, particularly the Polaris and Minuteman programs. Defense Department expenditures on research and development for fibrous composite materials went from \$400,000 in 1958 to \$14,000,000 in 1967, a growth rate of about 50 percent per year.⁽⁵⁾

Part of this growth can be attributed to the report of a new high strength, high modulus fiber developed by Texaco Experiment, Inc. in 1959. This new fiber, formed by the chemical vapor deposition of boron on a fine tungsten wire core, marked the beginning of the development of advanced reinforcement fibers and signaled the advent of improved composites. The boron fiber was followed by the development of graphite, silicon carbide, Kevlar®, alumina, and other advanced fibers. Of particular significance is the improved high temperature characteristics of these fibers (except Kevlar®) as compared to glass. The availability of these new high temperature, high modulus fibers has created many new applications for resin-based composite systems in military and aerospace applications. Applications of these materials have expanded to commercial areas as material and manufacturing costs have been reduced.

The invention of the boron fiber also marked the beginning of a new class of composites -- metal matrix composites. Prior to this time, potential metal processing and application temperatures had precluded the use of fiberglass as a reinforcement. A constant demand for ever higher temperature and strength capabilities, brought about by increased aircraft performance and space vehicle re-entry conditions, had pushed the application of standard aluminum alloys to their limit. The availability of boron, graphite, and silicon carbide fibers with their excellent high temperature mechanical properties, made the development of metal matrix composites possible.

CHARACTERISTICS OF COMPOSITE MATERIALS

As defined, a composite material is a combination of reinforcement fibers and a matrix material (the medium into which the fibers are embedded). The selection of the various fibers and matrices to apply to a specific composite system depends on the intended application, materials compatibility, and desired composite properties. Other factors that must be considered are materials costs and fabrication technology and costs. The following is a description of some of the characteristics of the fibers, matrices, and composite systems in widespread use today.

Fiber Materials

The fiber types available in commercial quantities for selection as a composite reinforcement currently consist of glass, carbon-graphite, aramid (Kevlar®), boron, silicon carbide, and alumina. Other fibers being developed include silicon carbide and silicon nitride whiskers and boron nitride.

The fibers all have similar general characteristics of low density, high strength, and moderate to high modulus of elasticity (modulus of elasticity is a measure of a material's stiffness). They come in different forms depending on manufacturing technique and application. In general, glass, graphite, and Kevlar® are supplied as bundles of very small diameter continuous filaments which have the appearance and some of the handling characteristics of textile yarns, i.e., they can be spooled and woven into mats or fabrics. Boron and silicon carbide fibers have a relatively large diameter and are supplied as single filaments in continuous lengths. These filaments are analogous to metal wire, and standard textile handling practices, such as weaving cannot be performed as readily. Silicon carbide is also supplied in the form of whiskers which are extremely small diameter, short-length fibers. Because of their small sizes they cannot be

handled like textile fibers or metal wires. Table 3-1 summarizes some of the important physical characteristics of the commercial and developmental fibers. A clear example of the advantage that the low density, high strength fibers offers over conventional materials is shown in Figure 3-1. The graph displays the relative specific strength and specific modulus of elasticity values (tensile strength and modulus of elasticity normalized by dividing by fiber density) for the various fibers compared to conventional aluminum, and steel. The information for the developmental fibers is not complete and is subject to change as development progresses.

Glass Fibers--

Glass fibers are the most common of the current reinforcement fibers. The major attributes of glass fiber are low density, high strength, and low cost. The major drawbacks to glass are its relatively low modulus and poor high temperature characteristics. The modulus of reinforcement grade glass fiber ranges from 10.5×10^6 pounds per square inch (psi) (E-glass) to 12.5×10^6 psi (S-glass). This range is comparable to the moduli of the metal matrix materials of interest (aluminum, magnesium, and titanium), but considerably higher than that of the plastics, which are typically less than 1×10^6 psi. For these reasons, glass is essentially restricted to plastic matrix reinforcement applications. One exception is the potential use of glass reinforcement in a lead matrix to form lead anodes for large-scale lead-acid batteries used in submarines.

Two forms of glass fiber are currently produced: continuous fiber and staple discontinuous fiber. Both forms are made by similar production techniques up to the drawing stage. The major constituents of E-glass are silicon dioxide, aluminum oxide, and calcium oxide. The S-glass formulation substitutes magnesium oxide for calcium oxide as a major ingredient. Both formulations contain controlled amounts of other minor ingredients including the oxides of boron, potassium, titanium, and iron.

Continuous fibers are mechanically pulled from the melt through a multiplicity of small orifices in the bottom of the melting crucible by gravity feed. As the fibers are withdrawn, they are quenched in a water

TABLE 3-1
TYPICAL PROPERTIES OF REINFORCEMENT FIBERS

	Glass		Graphite		Aramid Kevlar® 49	Boron	Silicon Carbide	Alumina FP	Silicon Carbide Whiskers
	E	S	High Strength	High Modulus	Pitch				
Density, g/cc on H ₂ O in	2.55 0.092	2.49 0.090	1.75 0.083	1.88 0.066	1.99 0.072	2.48 0.090	3.27 0.12	3.95 0.14	3.15 0.11
Tensile Strength, × 10 ³ psi	500	665	400	270-320	300	510	465	200	1,000-4,000
Tensile Modulus, × 10 ⁶ psi	10.5	12.5	30	50-70	55	58	58	55	70-120
Elongation at Break, %	3.0	--	0.4-1.2	--	0.5	0.8	--	0.4	3-4
Coefficient of Thermal Expansion in/in/°F × 10 ⁻⁶ (longitudinal direction)	2.8	1.6	-0.3	--	0.5 33*	2.7	2.7	--	--
Typical forms	strands, roving chopped, mats	strands, roving chopped, mats	strand, roving chopped, mats	strand, roving chopped, mats	strand, roving chopped, mats	continuous unid filament	continuous unid filament	continuous unid filament length to diameter of greater than 10:1	short length fiber
Single Fiber Diameter microns inches × 10 ³	3-20 0.1-0.8	8-13 0.3-0.5	6-12 0.2-0.5		12 0.5	100, 140, 200 4.0, 5.6, 8.0		25	<1-3 <0.04-0.1
* Radial Direction									
References	27	6	1, 2, 6, 29		1, 33	32	1, 32	1, 6	1, 6

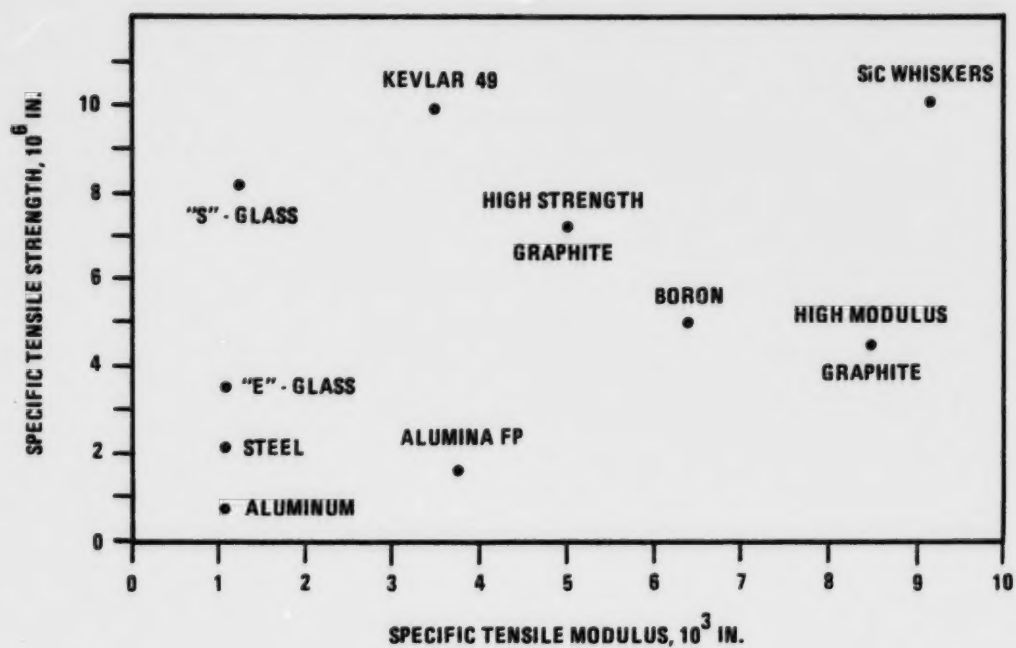


FIGURE 3-1 SPECIFIC TENSILE STRENGTH AND MODULUS OF REINFORCING FIBERS (TENSILE STRENGTH OR MODULUS DIVIDED BY DENSITY).

spray, coated with a protective and lubricating binder (size), gathered together in a bundle called a strand, and spooled. A strand typically contains 204 individual glass filaments or some multiple of this number. The individual filaments may range from about 3 to 20 microns (1×10^{-4} to 8×10^{-4} inches) depending on orifice size and drawing speed. Staple fibers are produced by passing a jet of air across the orifices as the fiber emerges, causing the fibers to break up into 8- to 15-inch lengths. These fibers are collected on a rotating drum, sprayed with a binder, and gathered into strands.

These continuous and staple fiber strands are usually further processed to form roving (a collection of 12 to 120 continuous strands with 60 being typical), chopped fiber, mats, and woven fabrics. Chopped fibers are typically 1/4 to 2 inches in length. The major U.S. producers of reinforcement grade glass fiber are Owens Corning Fiberglass Company and PPG Industries.(3,5)

Graphite Fibers--

A graphite fiber actually contains a mixture of amorphous carbon and graphite that has a hexagonal crystalline structure. The relative amounts of the two constituents depend on the time-temperature history of the forming process. The higher the time-temperature exposure the greater the degree of graphitization. The process also has a direct effect on strength and modulus. As the amount of graphite increases, the modulus increases and, in general, there is a corresponding reduction in strength. The predominant ingredient in the current commercial fibers is carbon; however, "graphite" is the industry-preferred term for this fiber.

Graphite fibers are produced from an organic fiber called a precursor. The three most popular precursor fibers are rayon, polyacrylonitrile (PAN), and pitch. Commercial graphite produced in the 1960's was based on the rayon precursor. The process consisted of heat treating rayon fibers in an inert atmosphere at temperatures up to 2,800°C. During the heating cycle, the fibers were stretched by applying a tensile load to align the rather disordered array of graphitic layer planes parallel to the fiber axis.

In the 1970's, the rayon precursor gave way to the PAN fiber as the predominant precursor for commercial graphite fibers. The PAN fiber is a linear polymer consisting of a carbon chain with attached carbonitrile groups. The first step in the process to produce a graphite fiber from the PAN precursor is to convert the linear structure into a "ladder" type structure. This process involves heating the fiber under tension in an oxidizing atmosphere at a temperature of 205° to 240°C for up to 24 hours. The fiber is then heated in an inert atmosphere at temperatures ranging from 1,400° to 3,000°C. The maximum treating temperature and time influences the degree of graphitization and, in turn, the properties of the fiber. For example, a heat treating temperature of 1,400°C produces a fiber with a modulus of about 30×10^6 psi, and a 60×10^6 psi modulus fiber is produced when a heat treating temperature of 1,980°C is used.

Recently, commercial quantities of graphite fibers have become available that are produced from pitch-based fibers. The pitch-based graphite fibers are produced from a liquid pseudocrystalline phase of petroleum or coal tar pitch called mesophase. The mesophase is formed in pitch after heating for up to 40 hours at 400 to 500°C. The viscous mesophase pitch has a considerable degree of molecular order. This pitch is then spun through an orifice to form filaments. The spinning process tends to align the ordered carbon-rich molecules along the filament axis. These highly aligned filaments are thermoset at relatively low temperatures and then heat treated at temperatures up to 3,000°C in an inert atmosphere.

The pitch-based process is in the early stages of commercialization. This process has the potential for becoming the predominant commercial process because of inherent low cost. Pitch, as a by-product of the petrochemical industry, is a relatively low cost raw material compared to rayon and PAN. The pitch-based graphitization process also gives higher yields of fiber per pound of raw material. The yield of graphite fiber from rayon, PAN, and pitch is approximately 26, 65, and 90 percent,

respectively. The more favorable yield for the pitch is primarily due to the higher ratio of carbon atoms to other atoms in the raw material.

The principal U.S. manufacturers of graphite fibers are Avco, Celanese, Great Lakes Carbon, Hercules, Stockpole Carbon, and Union Carbide.

Individual graphite fibers range in diameter from about 6 to 12 microns (2×10^{-4} to 5×10^{-4} inches) in diameter, or about the same size as individual glass filaments. Because these small fibers are difficult to handle, the graphite is gathered into bundles (tows) and wound onto spools. The tow contains about 1,000 to 160,000 individual fibers. The graphite tows, can be further processed to produce chopped fiber, mats, and woven fabrics.

Unlike glass, graphite has a high modulus of elasticity and excellent high temperature characteristics when protected from the atmosphere in a composite. For this reason, graphite has applicability to other matrix materials in addition to plastics. Graphite is particularly promising as a reinforcement fiber in aluminum matrix composites. Graphite fiber is used with a carbon matrix to produce an all-carbon composite that has the highest temperature capabilities of all composites (up to 3,100°C).

Kevlar® 49 (Aramid) Fibers--

Kevlar® 49 is one of a family of aromatic polyamide fibers (generically known as aramids) produced by E. I. Du Pont de Nemours & Co., Inc. It has the highest tensile strength ($>500 \times 10^3$ psi) and modulus of elasticity (18×10^6 psi) of the family and is the only one used primarily for composite applications. The fibers are spun from a poly-p-benzamide polymer above 500°F.⁽⁴⁾ Manufacturing details are proprietary but are assumed to be similar to other organic fiber processes except for starting materials and temperature.

The individual fibers are long and continuous and, like glass and graphite, are available in strands, rovings, chopped fibers, and woven fabrics. Also like glass, Kevlar's® limited high temperature capabilities primarily restrict it to organic resin composite applications. An exception is that Kevlar® 49 is being examined as a potential reinforcement for lead anodes in lead-acid submarine batteries.

Boron Fibers--

The application of reinforcement techniques to metals was made possible by the development of boron fibers, the first of the so-called advanced fibers. Like glass, boron fibers have high tensile strength (about 500×10^3 psi) but, more importantly, they have almost six times the modulus of glass and excellent high temperature characteristics. Boron is primarily used as a reinforcement in aluminum and magnesium, although it can be and is used with plastic resins as well. The major drawback to boron fiber is cost, which is currently about \$200 per pound.

Boron fiber was first produced in 1959 by Texaco Experiments, Inc., and is currently produced by Avco and the Composite Technology Incorporated. It is produced by continuously drawing a small tungsten wire (5×10^{-4} inch diameter) through a reactor tube containing a mixture of hydrogen and boron trichloride. The tungsten filament is resistance heated inside the reactor causing the boron trichloride to be chemically reduced at the hot filament surface and producing elemental boron and hydrogen chloride gas. The boron deposits on the hot wire surface, the thickness depending on the residence time in the reactor. The boron filament is wound onto reels upon exiting the reactor with no further processing such as sizing necessary.

The filament is typically produced in diameters of 0.004, 0.0056, 0.008, and 0.010 inches. Because of their relatively large size and stiffness, the filaments are not bundled like glass, Kevlar®, and graphite.

For the same reasons, boron fibers cannot be woven in the same sense as textiles. Composite Technology, Incorporated did develop a continuously woven boron tape with boron fibers in the longitudinal direction and Kevlar® or fine stainless steel wire in the transverse direction.

Boron fiber is also produced on a carbon substrate by the same process described above, with a carbon monofilament substituted for the tungsten. Replacing the tungsten core with carbon reduces the density of the fiber by about 10 percent, but the major advantage is the potential for lower cost. The potential for lower cost stems from a 30 percent increase in boron deposition rate⁽⁴⁾ and the inherent lower cost of the core material. There are no probable cost reductions through economies of scale for tungsten core fibers because tungsten wire is already produced in sufficient quantities for other applications. On the other hand, there is potential for such cost reductions for carbon fiber because of its increasing use in composites.

One drawback to the boron fiber is its tendency to react adversely with some of the metal matrix alloys at elevated temperatures. Reactions between the fiber and matrix reduces the fiber properties or, in the extreme, destroys the fiber. Such reactions prevent the use of boron with titanium and limits the applicability of boron as a reinforcement for aluminum. The degree of reaction between aluminum and boron depends on the time-temperature history of the couple. In general, fabrication or use temperatures above 500°C should be avoided and exposure times between 400 and 500°C should be minimized.^(7,8,9) To alleviate the reactivity problems, boron fibers have been fabricated with a variety of protective coatings.

One such fiber is Borsic® which is being produced commercially by Composite Technology, Incorporated. This fiber is produced by adding a thin coating (about 0.0001 inch) of silicon carbide onto the boron filament. The coating is applied by chemical vapor deposition in a second reactor following the main boron reactor. In this case a mixture of

® Registered trademark of Composite Technologies, Incorporated.

hydrogen and a methylchlorosilane is used that deposits silicon carbide on the hot boron surface. The hydrogen does not enter into the reaction, but its presence improves the quality of the coating.

A boron carbide coating developed in France is also used to protect boron. These fibers have the potential for applications in a titanium matrix. The coating is applied by chemical vapor deposition using a mixture of a hydrocarbon, boron halide, and hydrogen.⁽⁹⁾

Silicon Carbide Fibers--

Silicon carbide fibers were developed in 1966 by the General Technologies Corporation under contract to the Air Force Materials Laboratory. The fibers are currently being produced by Avco. The silicon carbide fiber is similar to the boron fiber with respect to the manufacturing process, mechanical properties, and size and handling characteristics. The great interest in silicon carbide as compared to boron stems from improved high temperature properties, reduced reactivity with metals, and, potentially, much lower cost.

Silicon carbide filament is produced by chemical vapor deposition in reactors essentially identical to those used for boron fiber. As with boron, a resistance-heated tungsten or carbon fiber is pulled through the reactor. The reaction compound is methylchlorosilane. Hydrogen is added to improve the quality of the silicon carbide although, theoretically, it is not required by the reaction. The silicon carbide is deposited on the hot substrate surface. This process has the potential for producing silicon carbide at lower cost than boron. The principal reaction chemical methylchlorosilane, is more than two times less expensive than boron trichloride and the silicon carbide deposition rates are higher than that of boron.

Silicon carbide has exhibited less reactivity with metals at high temperatures, improved strength retention at temperatures over 1,000°F, and less reactivity with metals as compared to boron. However, there are

reactivity problems between silicon carbide and titanium (a primary matrix metal for high temperature applications). Some significant reductions in reactivity with titanium have been observed when using a silicon carbide fiber with a carbon-rich outer layer.

Alumina Fibers--

A commercially available polycrystalline alumina fiber has been developed by E. I. Du Pont de Nemours & Co., Inc. This fiber, called alumina FP, is spun from an aqueous gel of aluminum hydroxychloride ($\text{Al}_2(\text{OH})_5\text{Cl}$). The fiber is dried and then heat treated to form a refractory oxide yarn.⁽⁴⁾ This fiber has excellent high temperature characteristics and is suited for reinforcement of some of the high temperature nickel and iron base super alloys as well as magnesium and aluminum. Alumina FP is a continuous, round, 100 percent alpha alumina fiber having a diameter of about 25 microns (1×10^{-8} inches).⁽¹⁰⁾ It is supplied in a yarn form that is easily handled. Its particular advantages are good strength properties (moderate tensile strength of about 200×10^3 psi), excellent retention of properties at elevated temperatures (over $1,000^\circ\text{C}$), and chemical inertness. The main drawback to the fiber is its high specific gravity of 3.95 as compared to other reinforcement fibers. However, some of its attributes, such as inertness and high temperature strength retention, outweigh the disadvantage in certain applications, particularly when used with the high weight super alloys.

Whiskers--

Whiskers are defined as a single crystal in a fiber form having a minimum length to diameter ratio of 10 to 1. Their typical diameters range from less than 1 micron to 3 microns. Their outstanding characteristics are the high strength properties they exhibit in comparison to bulk materials. Investigators have measured silicon carbide whisker tensile strength values in excess of 4 million psi and modulus values over 100 million psi.⁽¹⁰⁾

The reason for the increased strength stems from the near perfection of the whisker's internal and surface structure. A bulk material contains a multiplicity of grain boundaries, voids, and dislocations, any one of which may initiate a crack and subsequent material failure when a load is applied. The probability for a stress-concentrating defect to be present in a whisker is greatly reduced compared to the bulk material because of near perfect structure and small size. As the size of the whisker is decreased, there is a corresponding decrease in the probability of a defect to be present. This has been demonstrated by strength tests which show that fiber tensile strength increase as the fiber diameters decrease. Another attribute to the whisker form is its relatively high elongation (3 to 4 percent) before fracture.⁽¹⁰⁾ This is almost a fourfold increase over the high modulus graphite, boron, and silicon carbide bulk fibers. The improved elongation increases the whisker's toughness and handleability.

The major drawback to whiskers in composite applications has been the difficulty in efficiently utilizing their improved properties. One of the major factors in producing good quality composites is uniform distribution of the fibers. It is also important that each fiber is surrounded by matrix and that there is a good fiber-matrix bond. All of these factors are difficult to achieve with whiskers and have been met with only limited success to date.

A wide variety of materials have been prepared as whiskers, including: copper, iron, aluminum oxide, magnesium oxide, graphite, aluminum, nitride, silicon nitride, boron carbide, and silicon carbide. The one that currently shows the most promise for composite applications is silicon carbide. This fiber was first produced commercially by Thermokinetic Fibers, Inc. in 1962. The current U.S. producer is the Silag Division of Exxon Enterprises, Inc. Silag developed a process to produce silicon carbide whiskers from rice hulls; a process which has excellent potential for low cost, possibly as low as \$10 per pound.⁽⁴⁾ The rice hull has a high content of both silica and carbon. Pyrolysis of the hulls high grade whisker material. Currently, the useable whisker fraction of the silicon carbide produced is approaching 90 percent.⁽¹¹⁾

Matrix Materials

The matrix material comprises the body of the composite. Its role, beyond providing the bulk of the structure, is to encapsulate and hold the fiber reinforcements in place and transfer the applied loads to the fibers. The prime candidate matrix materials are the lightweight structural materials like plastics, carbon, and the lightweight metals. Many of these materials already have excellent structural properties but there is always the need to extend these capabilities, particularly to extend a material's elevated temperature limits. There is also interest in fiber reinforcement of some of the more dense materials such as the super alloys and ceramics for specific applications.

There are two main classes of plastic resins: thermoset and thermoplastic. Thermoset resins are usually liquid or semi-liquid at room temperature before setting (curing). With the action of a catalyst, heat, or pressure or some combination of all of these, the resin undergoes an irreversible chemical transformation (cure) and the resin becomes a solid. Once cured the resin cannot be remelted or returned to the uncured state. A thermoplastic is usually a solid or solvent-based solution at room temperature. The solid form is made to take on a shape or form by melting the solid and molding the hot resin. After cooling, the solid plastic can be returned to the liquid state by reheating. The solvent-based resin is solidified by solvent evaporation.

The principal thermoset resins used for composite materials are polyesters, epoxies, phenolics, vinyl esters, polyimides, and urethanes. The thermoplastics used for composites include nylon, polypropylene, thermoplastic polyester, polystyrene, polysulfones, and polycarbonates.

The metals that have received most of the attention for development of composite systems are aluminum, magnesium, and titanium. Other metals that have been utilized include copper, lead, and more recently, the super alloys.

Typical properties for the matrix materials of interest are included in Table 3.2 in the following section.

Composite Materials

Up to this point we have described the characteristics of the reinforcements and matrices. When the two materials are combined, a third material is created that has come of the characteristics of each of the components. A composite generally has the look and feel of the nonreinforced matrix material; it is often not evident that the fibers are present. At the same time, the well-designed and fabricated composite will have greatly enhanced physical properties as compared to the matrix. This is brought about by the transfer of a portion of the properties of the fibers to the composite as a whole. As previously stated, when a load is applied to a composite, the fiber's role is to carry the major portion of the load and the role of the matrix is to transfer the load to the fiber. Another important factor is the role of the interface or bond between the matrix and fiber. Localized stresses are usually highest at, or near, this interface. The physical and chemical characteristics of the interface must be such that load transfer from the matrix to the fibers is supported. In the case of the glass fiber and resin system, interfacial conditions are improved by the addition of a coupling agent to the glass fiber surface. Silanes have been the most frequently used coupling agents for glass fibers. Inorganic coatings have been used with graphite and boron to improve interfacial characteristics between the fiber and metal matrices.

The manner in which the matrix, interface, and fiber fulfill their respective roles in the composite structure have been examined by a number of analytical models and failure theories. Experimental data have verified that certain composite parameters can be predicted. The modulus of elasticity of a unidirectional continuous fiber composite can be predicted with reasonable precision using the following "rule of mixtures" relationship:

$$E_c = E_f V_f + E_m V_m$$

where E_c = Composite modulus

E_f and E_m = Fiber and matrix modulus, respectively

V_f and V_m = Fiber and matrix volume fractions,
respectively

Similar but somewhat more complex equations have been derived to predict tensile strength and other mechanical properties for composites having continuous and short fiber reinforcements with various orientations.

A composite structure is often thought of as a two-component system: the matrix and one type of reinforcement fiber. There is another type of composite, commonly referred to as a "hybrid" composite, which contains two or more fiber types; for example, a mixture of glass and graphite fibers. (There are composites which utilize both chopped and continuous forms of the same fiber. These are not generally called hybrids.) The hybrid concept is often applied where a particular structure may require reinforcements to strengthen one area and stiffen another. Glass fibers are used in the high strength area and high modulus graphite is used in the area requiring stiffening. Another important application of hybrids is cost reduction. It may be possible to replace high cost reinforcements in noncritical areas of a structure with lower cost fibers such as glass.

Typical properties of some of the common composite materials are given in Table 3-2. Properties of selected matrix materials are included for comparison purposes.

MANUFACTURING METHODS

The principal goal of successful composite fabrication is to obtain a finished product with the fibers placed in the desired location along with correct orientation and distribution. It is also important that the fabrication process does not damage the fibers and that good bonding exists between the matrix and fiber to allow efficient load transfer.

TABLE 2.2

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TABLE 3-2 (cont. Inued)
TYPICAL PROPERTIES OF COMPOSITE MATERIALS

	Aluminum Graphite (Pine)		Aluminum Graphite (Pitch)		Aluminum Boron		Magnesium Graphite		Titanium BORSiC		Aluminum Silicon Carbide Whisker		Carbon Graphite		Unreinforced Aluminum Magnesium		Titanium	
	40	50	50	50	50	50	30	45	45	20	50	50	50	50	---	---	---	---
Fiber Content, Volume Percent																		
Density, g/cu cm	2.4	2.4	2.4	2.4	2.5	2.5	1.8	3.6	3.6	2.8	1.7	2.7	1.7	1.0	4.4			
lbs/cu in	0.86	0.86	0.86	0.86	0.89	0.89	0.066	0.13	0.13	0.10	0.061	0.096	0.066	0.066	0.16			
Tensile Strength, Unidirectional $\times 10^3$ psi	120	155	155	155	200	200	74	184	184	50	15	20-40	20-40	20-40	180			
Tensile Modulus, Unidirectional $\times 10^6$ psi	30	50	50	50	34	34	43	32	32	15	6	10	6.5	6.5	16			
References	45	45	45	45	45	45	45	45	45	45	45	45	45	45	60	60		

In the early days of composite development, fabrication was accomplished by hand. In many cases hand operations are still used today still used today and are a major barrier to the development of some composite systems on a commercial scale. Hand operations are necessary in many instances to achieve the first goal: to place the fiber in the correct location, with proper orientation and distribution.

In some cases, a whole new manufacturing technology has emerged, such as the filament winding process; in others, existing technology has been adapted to fit composite fabrication needs. For example, a sheet metal stamping operation was modified to form composite sheet material; a composite process called thermal stamping.

Damage to the fiber due to reactions between the matrix and fiber has not been a problem in plastic composite systems. Mechanical damage to the fiber is always a threat and is a major consideration in the engineering design of the fabrication process. Bond integrity between the matrix and fiber has also not been a major problem with the plastic composite systems. When poor bonding has occurred because of inability of the matrix to "wet" the fiber surface, coatings (sizing) have been developed to enhance fiber wetting. This procedure has been successful in most cases and has not resulted large additions to costs.

The fabrication process goals for metal composite systems have not met with the same degree of success. Existing metal fabrication technologies have not been particularly adaptable to composites. One of the plastic composites technologies, filament winding, was tried with some success. As applied to metal composites, the process consists of winding a fiber onto a mandrel immersed in an electroplating bath. As the filament is wound onto the mandrel it is covered with electroplated metal which forms the matrix. The process is expensive and is limited to those matrices which are readily electroplated. Therefore, the emphasis has been to develop new technologies for metal composite fabrication. To date there has been only limited success particularly when cost is considered.

A major problem in the development of metal matrix composite systems has been the propensity for filament damage and poor bonding between the fiber and matrix. Fiber damage can result from mechanical force or from chemical reaction between the matrix and fiber. Fibers such as boron and silicon carbide are commonly used with metals and are large in diameter (up to 10×10^{-3} inches) in comparison to glass, graphite, and Kevlar®, which have individual fiber diameters that are about ten times smaller. These large fibers cannot be subjected to small bending radii without fracture. This places a severe limitation on the fabrication of complex shapes. For those processes requiring pressure, the pressures required are usually much higher than in plastic composite fabrication, up to 15,000 psi in some cases. Fabrication pressures can usually be reduced by increasing the fabrication temperature, but reactivity between the fiber and matrix may become a problem. The higher the temperature, the higher the potential for an adverse reaction. This problem has resulted in trade-offs between temperature and pressure and in application of coatings to the filament to prevent reaction. Borsic®, which is a silicon carbide-coated boron fiber, is an example of the application of such a coating.

The ability to achieve good bonding is also a major problem in metal matrix composite fabrication. A poor fiber-matrix bond prevents good load transfer from the matrix to the fiber, and the result is poor composite properties. Bonding is related to process temperature and the fiber-matrix chemical coupling. For best results, the matrix should wet the fiber. Again, coatings are the common solution to this problem. For example, aluminum does not readily wet graphite: the result being poor bonding and poor infiltration of the aluminum into the fiber bundle. The Aerospace Corporation has developed a titanium-boron coating for graphite which, when applied, allows good wetting of the graphite.

Another goal of the fabrication process is to produce a product with a high degree of consistency in its physical and engineering properties. A part or structure produced during one production run should be identical to one produced during another within reasonable and predictable limits. Unless this is so, the material cannot be efficiently used by design engineers, without incorporating large safety factors into products. The

more hand operations and material variability, the more difficult it is to achieve uniformity. Therefore, there is a strong impetus to minimize difficult to control manual operations and to expand automation in composite processing.

The following is a brief discussion of the major fabrication methods currently used for the various composite systems. Intensive development is continuing to improve these methods or to find new ones to increase output, lower cost, and improve composite uniformity.

Plastic Matrix Composite Fabrication

There are two main routes to the fabrication of a finished resin matrix composite part. The first is to combine the raw materials and the resin and fibers, and fabricate them directly into the finished part. The second is to form an intermediate from the raw materials, then fabricate the finished part from the intermediate. One of the intermediates called a "prepreg" is made by infiltrating fiber strands, mats, or woven fabric with resin and then partially curing the resin. The resin infiltration is accomplished by drawing the strands through liquid resin tanks or by immersing mats or cloth into the tanks. The prepreg material is usually in the form of long tapes up to 3 inches wide (narrow prepreg) or wide sheets up to 48 inches wide (broad goods). The partially cured prepreg is a relatively dry, tack-free material that is easy to handle. A multiplicity of prepreg pieces are used to form the final part by cutting the prepreg to size, placing it in the mold, and completing the wiring process. The prepreps are manufactured by some of the fiber manufacturers, such as Avco and Hercules or by independent companies such as Fiberite, U.S. Polymeric, and Narmco, which specialized in prepreg fabrication.

A second intermediate form is sheet molding compound (SMC) consisting primarily of fiber-reinforced polyester. The SMC fabrication process consists of applying a layer of resin on a backing sheet onto which a layer of chopped fiber and continuous strands are applied. A cover layer of resin with backing sheet is applied over the fibers. The sheet is then rolled and shipped to the parts fabricator. The final part is fabricated

by cutting the sheet to size and then forming the composite into the part by compression molding or thermal stamping. This operation conforms the SMC to the desired shape and cures the resin.

The third type of intermediate is a thermoplastic molding compound. The compound is formed by feeding a mixture of thermoplastic resin and chopped fiber, continuous fiber roving, or a mixture of the two into a heated extrusion machine. The thermoplastic is melted, mixed with the fibers, and extruded through a heated extrusion die to form a rod-shaped reinforced intermediate. The intermediate can then be used as feedstock for an injection molding machine to fabricate finished parts.

The major plastic composite fabrication techniques used to form parts either directly or through intermediates are as follows:

- Low-pressure molding
- Compression molding
- Thermal stamping
- Extrusion
- Injection molding
- Filament winding

Low-Pressure Molding--

Low-pressure molding techniques were among the first methods used for fiberglass composites and are adaptable to the more advanced fibers. The general technique consists of placing by hand glass fiber mat or fabric on a shaped mold in layers. Each fiber layer is coated with resin in succession. This is called contact molding. The quality of the part is quite dependent on the laborer who must distribute the resin correctly and squeeze out the entrapped air. The fiber content usually ranges from 30 to 40 percent by weight.

Variations of this method include vacuum bag, pressure bag, and autoclave molding. These methods involve the hand layup of precut prepreg material which is placed in a flexible bag. In the case of the vacuum bag,

the bag is evacuated with a vacuum pump during cure. The applied pressure is limited to 12 to 14 psi. The pressure developed on the bag eliminates air, voids, and excess resin. The pressure bag technique involves applying a uniform pressure on the outside of the bag. A typical pressure bag method is to use an autoclave, a large cylindrical pressure vessel that can be heated. The pressure bag containing the composite layup is placed inside the autoclave with applied heat and pressure, typically 180°C at pressures up to 100 psi. The autoclave processing yields composites with low void content, improved uniformity, and fiber contents from 40 to 60 percent by weight.

Low-pressure molding techniques in general do not require expensive tooling but are quite labor intensive due to the required hand operations. Another drawback is the long cure cycles that are usually required, in some cases up to 24 hours including the time in a post-cure oven.

Compression Molding--

Compression molding is often referred to as matched-die molding. The process consists of placing prepreg material between a pair of matched dies that are in the shape of the finished part. The mold is closed and placed in a hydraulic press with heated platens through which heat and pressure are applied to the mold. Because of heat transfer efficiency, the cure cycles are usually faster than autoclave curing. Pressures of up to 1,500 psi are typically used. Large automated matched-die molding machines are currently used by the automotive industry to fabricate component parts from SMC. These large machines are capable of cycling parts in minutes instead of hours.

Thermal Stamping--

Thermal stamping is a fast automated method for forming composite components that is analogous to sheet metal stamping. Composite prepreg sheet, typically thermoplastic or specially formulated SMC, is cut to shape

and placed on a preheating table next to the sheet stamping machine. The sheets are usually preheated with a radiant heater. The preheated sheets are automatically fed to the machine between open matched metal die platens. The die is rapidly closed to form and cool the part. The press is then opened and the part removed. The whole cycle lasts about 30 seconds.

Continuous Extrusion--

Continuous extrusion or pultrusion is a process which forms continuous, constant, cross-section shapes like "I" beams, rods, tubes, angles, and bar stock. A continuous feed of a bundle of fiber strands or rovings is pulled through a resin bath and then through a heated die which has the shape of the desired cross-section. The die removes excess resin, shapes the composite, and cures the resin. Additional cure or post-cure heat can be applied after the composite exits the die by radiant heating. The fiber content of pultruded shapes are typically 60 to 80 percent by weight.

Injection Molding--

Injection molding is a common plastics forming method consisting of forcing liquid resin into a mold under pressure. To make fiber-reinforced parts, chopped fiber is usually premixed with the resin prior to injection. It is possible to place fiber inserts into the mold prior to injection but this practice is not common. By proper mold design, some flow of the material can create preferential fiber alignment in certain areas of the part. The process is commonly used for molding thermoplastics where the preheated resin is injected into a cold mold. The process has been applied to thermosetting resins which have been specially formulated for injection molding. In this case the resin is injected into a hot mold.

A recently developed process called reaction injection molding (RIM) has been applied to the fabrication of composites. In this case the process is referred to as reinforced reaction injection molding (RRIM). In this process, separate streams of highly catalyzed urethane resin are

pumped to a high impingement mixing nozzle at or near the injection port of the mold. Chopped fiber is introduced at the nozzle. The resin cures in the heated mold to form a finished composite in less than 30 seconds.

Filament Winding--

Filament winding is one of the classic techniques for fabricating fiber-reinforced composite materials. An entire technology has developed around this process and includes special design considerations, new test methods, and the manufacturing technology. The composite is formed with fiber strands or roving that are continuously fed through a resin bath and onto a suitably designed mandrel which is usually a surface of revolution. Preimpregnated strands of fiber can be used to eliminate the need for a resin bath. The resin is cured on the mandrel and then the mandrel is removed. The winding technique allows the fibers to be oriented circumferentially, longitudinally, or at any desired helix angle. The part may consist of several layers of the same or different orientations, depending on the use load conditions. The product typically has fiber contents ranging from 60 to 90 percent by weight.

Filament winding has been used to fabricate rocket motor cases, missile bodies, pressure vessels, tankage, helicopter driveshafts, and rotor blades and tubing.

Metal Matrix Composite Fabrication

A number of processes have been tried over the years for fabrication of metal matrix composite materials which include diffusion bonding, liquid metal infiltration, electroplating, pultrusion, continuous casting, and powder metallurgy. Only two of these processes have significant use at the current time: diffusion bonding and liquid infiltration.

As with the plastic matrix fabrication techniques, an intermediate step is often used to prepare a preform material which combines the matrix and fiber prior to final fabrication. This facilitates the handling of the fiber and, in some cases, the bonding and infiltration of the fibers during final fabrication. The following is a discussion of these intermediate and final fabrication processes.

Diffusion Bonding--

Diffusion bonding, or as it is sometimes called hot pressure bonding, is the predominant process for fabrication of metal matrix composites. It is used for fabricating composites with both the large diameter fibers, such as boron and silicon carbide, and the small diameter graphite fiber. The process basically consists of applying heat and pressure to an alternating stack of matrix metal sheets and fibers. The heat and pressure cause the layers of metal to come together and interdiffuse to encapsulate the fibers.

The typical process for the formation of a boron-aluminum composite includes the following steps. The first step involves the preparation of a preform material which consists of winding a monolayer of boron filament on a sheet of aluminum wrapped around a drum mandrel. The boron is secured in place with a coating of adhesive binder. A number of these monolayers, depending on the desired thickness of the final product, are placed in a flexible vacuum bag. The bag is placed in a mold in a hydraulic press. As the mold is heated, the bag is evacuated, removing the adhesive binder as it vaporizes. When the correct temperature is reached, pressure is applied and held while diffusion takes place. Upon completion the mold is cooled and the part removed. Basically the same procedure is used for boron-magnesium and Borsic®-aluminum. The use of Borsic® allows somewhat higher mold temperatures and correspondingly lower pressures.

A procedure being developed by Avco involves using silicon carbide fiber in aluminum and operating the mold close to the melting point of aluminum, which will allow the diffusion pressure to be reduced by a factor of ten. A titanium carbide or titanium nitride coating is deposited on the silicon carbide prior to processing to facilitate the wetting of the fiber by the aluminum.⁽⁴⁾

A variation of the intermediate preform step is to plasma spray the aluminum matrix onto a monolayer of fiber. This process eliminates the organic binder used to hold the matrix and fibers together prior to diffusion bonding.

The aluminum-graphite couple involves liquid infiltration as an intermediate step and diffusion bonding for final composite fabrication. Initial problems encountered with molten aluminum not wetting graphite have been solved by precoating the graphite with a titanium-boron coating. This process was developed by the Aerospace Corporation. The production of the aluminum-graphite composite involves the fabrication of an intermediate by drawing a continuous titanium-boron precoated graphite strand through a molten aluminum bath. This wets and infiltrates the bundle with aluminum and forms a small preform aluminum-graphite rod. A composite part or structure is formed by consolidating a multiplicity of these rods by diffusion bonding, in a fashion similar to the boron-aluminum process.

Liquid Metal Infiltration--

Liquid metal infiltration involves infiltration of fiber preform with liquid metal in a mold. The process is primarily being used to form magnesium and aluminum matrix composites using alumina FP fiber as reinforcement. Molten magnesium readily wets alumina and spontaneously infiltrates fiber bundles. This is not the case with aluminum which does not wet alumina fiber. It has been found recently that sufficient wetting can be obtained by alloying a small amount of lithium with the aluminum.

The process begins by making alumina fiber tapes using an organic binder to hold the fibers in place. The tapes are laid up in the mold in the desired location and orientation. The mold is heated to vaporize the organic binder, and then liquid metal is injected into the mold by gravity or under pressure. After matrix solidification and cooling, the finished reinforced part is removed from the mold. The process is relatively simple

in terms of equipment needs and operation and has the potential to be a low-cost process.

Carbon Matrix Composite Fabrication

The fabrication of carbon matrix composites basically involves only graphite reinforcements. The common fabrication technique consists of impregnating a graphite fiber preform with carbonaceous material. Impregnation is done by a variety of techniques including the direct deposition of carbon by chemical vapor deposition or indirect methods that impregnate the fiber preform with carbonaceous material which is subsequently carbonized. A method that is currently used commercially consists of the liquid impregnation of a three-dimensional graphite fiber array with petroleum or coal-tar pitch. The pitch is then carbonized and heat treated under pressure. The liquid impregnation - carbonization - heat treat cycle is repeated until the fiber array is filled with matrix.

CURRENT USES

Applications

Composites applications have grown from the first use of fiberglass reinforced plastics in aircraft during World War II to the present-day wide diversity of applications in military and commercial products. In terms of numbers of applications and quantities, fiberglass reinforced plastics are the predominant material, but the emergence of the new high temperature, high modulus fibers in the 1960's and 1970's has caused the replacement of some glass with the new fibers and has extended the composite concept to metals and ceramics.

The advantages that composite materials offer compared to conventional materials are the driving forces that have maintained the continuing interest in composite applications over the years. Some of the advantages that the use of composites offer are:

- Weight - Designers can reduce structure weight through the use of composites in two ways. The first is to replace relatively heavy materials such as steel with lightweight reinforced metals or

plastics of comparable strength. Substituting composites can result in weight savings of over 80 percent based on specific gravity differences. The second is to replace structures made from conventional lightweight metals or plastics with composites having higher strength and stiffness. This type of substitution allows reductions in structure volume with corresponding reductions in weight.

- Temperature - Conventional metals, plastics, and ceramics lose strength and stiffness with increasing temperature. Reinforcement of these materials with high temperature fibers such as graphite, boron, alumina, or silicon carbide whiskers extends the practical use temperature, in some cases, practically to the melting point of the matrix.
- Design Flexibility - A composite material can be custom designed to fit the application. Control over materials combinations and fiber placement give the designer flexibility and the ability to optimize composite properties. The use of more than one type of fiber in a composite ("a hybrid") can reduce cost and improve performance. For example, relatively inexpensive glass fiber can be used throughout a structure to improve strength, and high modulus graphite fiber can be used only in those areas requiring increased stiffness.
- Corrosion Resistance - Fiber reinforced plastics exhibit a high degree of inertness during exposure both to the normal environment and to chemicals. The use of the corrosion-resistant composites significantly reduces long-term maintenance costs in many piping, storage tank, and chemical industry applications.
- Energy - The consumption of energy is affected in two ways by composites. The first is during manufacture of the product, and the second is during the use of the product. In many cases the use of a composite to replace conventional material results in a net energy saving during manufacture. For example, it takes about

8,000 Btu's to produce a cubic inch of magnesium or die cast aluminum and 5,000 Btu's for steel, whereas it takes only 3,000 to 4,000 Btu's for production of polyester and nylon and about 1,000 Btu's for polypropylene.⁽¹³⁾ The use of composites in cars, trucks, boats, aircraft and spacecraft reduces, through decreased weight, the energy required to propel the vehicles during their useful lives.

- Performance - The performance of composites in terms of strength, stiffness, toughness, and impact resistance is generally better than the conventional materials they replace, particularly when relative weights are taken into account. The sports equipment industry is a good example. Many users of composite golf clubs, tennis rackets, and sailboat masts feel that their composite equipment far outperforms any conventional material counterpart, so much so, that composites have been outlawed in some competitive sports.

The reasons for using composite materials varies somewhat according to the industry. The automotive and commercial aircraft and spacecraft industries are motivated to use composites primarily to conserve energy. The low weight and performance of composites provide the desired energy-saving advantage over conventional materials. The consumer products, appliance, construction, marine and business equipment industries are motivated to use composites to increase product durability and corrosion resistance, and to reduce maintenance requirements, and costs. Product weight is also a factor. Fiber reinforced plastic pipes and tanks are lighter than steel and easier to handle. A fiber reinforced suitcase is also lighter than a leather one, but more importantly, the composite suitcase is more durable at less cost. The military, sports equipment industry, and, to some extent, the marine industry are motivated to use composites primarily because of the improved performance of composites.

The driving force to replace the fiber used glass reinforcement with advanced fibers also varies according to the industry and is related to the reasons for using composites (assuming a significant price differential between glass and the advanced fibers). The automotive and aerospace industries, which are heavily dependent on energy costs, will expand the use of the lighter, higher performance advanced fibers as the tradeoff improves between increasing energy costs and fiber costs. The industries primarily interested in corrosion resistance, durability, low maintenance, and costs do not have a strong incentive to switch to the advanced fibers. In many cases, glass is "good enough," and in others the slight increase in performance or weight reduction by using advanced fibers is not justified by the increased costs.

In contrast, the military and the sporting goods industries are primarily interested in performance, and costs are not the major factor.⁽³⁾ These industries have both been the pioneers in the use of advanced fibers. It should be noted that in the sporting goods industry, the amount of advanced fiber used in each item is relatively small and the increased cost for the sports enthusiast has not been prohibitive. For example, the boron tennis racket contains about 0.15 ounce of boron worth about \$1.50. The major portion of the increased cost of the racket (about \$20) results from increased development and manufacturing costs.

The growth rate of composite applications during the last decade has been significant, but the spectacular growth rate that was predicted early in the period has not materialized. The two major barriers to growth, in terms of new applications and quantities, has been, and is currently, high fiber costs and manufacturing technology. The advanced fibers cost tens to hundreds of dollars per pound. The manufacturing processes are labor intensive and have many hand operations, which in some cases, tend to increase costs and slow production. It has been difficult to establish product specifications and inexpensive quality control procedures. These barriers have particularly impeded the growth of composite applications in the commercial sector where materials costs and automated manufacturing

methods are well established. Application growth in the military and aerospace industries is more advanced because high cost does not have the impact that it does in the commercial sector. A great deal of effort is underway in both the military and commercial sectors to develop improved manufacturing processes, material specifications, and quality control procedures. The consensus is that as these problems are solved, applications and production quantities will increase.

Composite applications are wide and varied throughout the military and commercial sectors, albeit the production quantities are low for most composites other than glass fiber reinforced plastics. Current applications for the various composite types listed by matrices and fiber types are given in Tables 3-3, 3-4, 3-5, and 3-6. Notation as to whether the application is in development or has advanced to the production stage is indicated by a "D" or "P", respectively.

The following is a description of some of the major applications of composites in commercial and military products.

Commercial Applications - Reinforced Plastics--

Automotive--Current uses of composites in automobile manufacturing are restricted to fiberglass reinforced plastics. There is, however, a continuing research and development effort in the industry to utilize composites containing more advanced fibers, particularly graphite and, to a lesser extent, Kevlar®. A highlight of this research was the fabrication of an all graphite experimental 1979 LTD. The car, fabricated by Ford for an estimated cost of \$3.5 million, has a graphite fiber reinforced body, frame, and chassis parts (a total of 160 in all) and weighs 2,500 pounds, about one-third less (1,250 pounds) than a standard LTD. The experimental full-size car achieved a fuel consumption rate of 24.7 mpg an improvement of about 30 percent as compared to the standard LTD.⁽¹⁴⁾ Although this project proved that such a car could be built with advanced composites, and

TABLE 3-3
REINFORCED PLASTICS (THERMOSETTING) APPLICATIONS

Plastic Matrix Composites Thermosetting Resins	Military				Commercial								
	Space	Aircraft	Naval	Land Equipment	Automotive	Sports	Marine	Industrial	Aircraft	Space	Medical	Power	Consumer Products
<u>Polyester</u>													
Glass		P	P		P	P	P	P	P				P
Graphite				D	D								
Kevlar®			D	D			P	P					
Boron													
Hybrids			D		D		P						
<u>Epoxy</u>													
Glass					P	P	P	P	P	P		P	
Graphite		P	D	D	D	P		P	P	P	D		D
Kevlar®		P				P		P	P	P		D	
Boron		P				P		P	P	P			
Hybrids		P	D		D	P		D	D	P			
Phenolic													
Glass		P						P					
Graphite		P											
Kevlar®													
Boron													
Hybrids													
<u>Polyimide</u>													
Glass													
Graphite	D	D	D						D	D			
Kevlar®													
Boron	D												
Hybrids													
<u>Urethane</u>													
Glass													
Graphite													
Kevlar®													
Boron													
Hybrids													
<u>Vinyl ester</u>													
Glass													
Graphite													
Kevlar®													
Boron													
Hybrids													

D = Development in progress (early development to prototype).
P = Major components have reached production.

TABLE 3-4
REINFORCED PLASTICS (THERMOPLASTIC) APPLICATIONS

Plastic Matrix Composites Thermoplastic Resins	Military			Land Equipment	Commercial								Consumer Products	
	Space	Aircraft	Naval		Automotive	Sports	Marine	Industrial	Aircraft	Space	Medical	Power		
Nylon														
Glass									P			P		P
Graphite														
Kevlar®									P					D
Boron														
Hybrids														
Polysulfone														
Glass									P					P
Graphite														
Kevlar®														
Boron														
Hybrids														
Polypropylene														
Glass									P			P		P
Graphite														
Kevlar®														
Boron														
Hybrids														
Polystyrene														
Glass									P			P		P
Graphite														
Kevlar®														
Boron														
Hybrids														
Polycarbonate														
Glass									P					P
Graphite														
Kevlar®														
Boron														
Hybrids														

D = Development in progress (early development to prototype).

P = Major components have reached production.

TABLE 3-5
METAL MATRIX COMPOSITES APPLICATIONS

Metal Matrix Composites	Military				Commercial				
	Space	Aircraft	Naval	Land	Automotive	Sports	Marine	Industrial	Consumer Products
Aluminum									
Alumina FP			D						D
Boron*	P	D	D					D	
Graphite	D	D	D	D		P			D
Silicon Carbide	D	D	D	D					
Whiskers	D	D	D	D					
Magnesium									
Alumina FP			D						
Boron	D								
Graphite	D								
Titanium									
Boron*			D						
Silicon Carbide	D?	D							
Copper									
Graphite			D						D
Lead									
Alumina FP			D						D
Glass			D					D	
Graphite			D						
Super Alloys									
Alumina FP									
Silicon Carbide		D							
Tungsten			D						

D = Development in progress (early development to prototype).

P = Major components have reached production.

* Boron includes boron fibers coated with silicon carbide (Borsic®) and boron carbide coated boron.

TABLE 3-6
CARBON AND CERAMIC MATRIX COMPOSITE APPLICATIONS

	Military					Commercial									
	Carbon Matrix Composites	Space	Aircraft	Naval	Land	Automotive	Sports	Marine	Industrial	Aircraft	Space	Medical	Power	Consumer Products	
<u>Carbon</u>															
Graphite		D		P						P		D	D	D	
<u>Ceramic Matrix Composites</u>															
<u>Boron Nitride</u>															
Boron Nitride		D													
<u>Silica</u>															
Boron Nitride		D													
Silica		P													
<u>Silicon Carbide</u>															
Silicon Carbide Whiskers		D													
Silicon Nitride Whiskers		D													
<u>Silicon Nitride</u>															
Silicon Nitride Whiskers		D													
<u>Glass</u>															
Alumina FP		D													
Graphite		D													
Silicon Nitride Whiskers		D													

D = Development in progress (early development to prototype).
P = Major components have reached production.

that it performed well, the economics of using advanced composites are not yet suitable for using these materials in mass production.

The best known current application of composites in the auto industry is the Chevrolet Corvette. Since its introduction in the mid-1950's, the Corvette's exterior body has been fabricated by compressive molding of SMC.

The 1979-80 models of U.S. cars utilize about 190 pounds of plastics per car on the average, and approximately 10 percent of this total is fiber reinforced plastics.⁽¹⁵⁾ The 1979 cars and trucks utilized 628 different 93 in the passenger compartment, 61 electrical, and 20 in engine drive systems.⁽¹⁶⁾ Some of these applications are listed below:⁽¹⁷⁾

Body Panel and Exterior Components

Air deflectors
Body pillar
Fender extension
Fender liners
Grille opening panels
Tilt front ends (truck)
Rear quarter panels
Window mechanism

Engine Drive Systems

Transmission parts
Clutch release lever

Electrical

Coil bobbins
Computer housings
Distributor cap and parts
Ignition housings
Junction boxes
Lamp sockets

Interior

Bench seats
Floor consoles
Instrument panels and parts
Bucket seats
Steering column covers
Structural supports

Under Hood

Air conditioner housing and parts
Battery trays and retainer parts
Brake cylinder
Fan blade
Oil suction tube
Fan shroud

Most of these applications are for nonload-bearing parts, but a major load-bearing application is being introduced in the 1981 Chevrolet Corvette. An eight-pound single leaf transverse rear spring made from fiberglass reinforced epoxy is used to support up to 3,500 pounds of static

and dynamic load. This single composite part replaces a 45-pound multi-leaf steel spring, and tests indicate that it is more durable than the steel unit. Considerable effort has been expended in the development of fiberglass epoxy drive shafts produced by filament winding techniques. The trend towards front wheel drive has diminished the potential for composite driveshaft applications in the passenger car, but such applications in trucks are expected in the near future.

commercial aircraft applications for interior and exterior components are listed below:

<u>Interior</u>	<u>Exterior</u>
Window reveals	Wing to body fairings
Overhead and side panels	Landing gear doors
Floors	Leading and trailing edges
Lavatories	Access doors
Galleys	Radomes
Bulkheads	Engine nacelles, cowlings, and pylons
Pressure bottles for escape slides	Rotor blades
Air ducting	Propellers
Seat pedestals	

The aircraft using these applications include the Douglas DC-10, Lockheed L1011, Boeing 727 and 747, the deHavilland DHC-7, and the Sikorsky S-76 helicopter. The use of Kevlar® in the L1011 resulted in a 25 to 30 percent weight savings over the use of glass, an 800-pound weight saving overall. Kevlar® reinforced plastics used in the deHavilland DHC-7, for main flap leading edges, avionics bay, and interior panels, save 200 to 300 pounds over glass reinforced plastics.

NASA Langley's (aircraft energy efficiency) ACEE program is devoted to the development of major composite primary structure components for commercial aircraft applications. In six separate programs, where emphasis is placed on putting parts in production, parts are being designed as replacements on commercial aircraft now in service. A honeycomb/graphite-skin elevator is being developed by Boeing under the program to replace the aluminum metal-bonded version used on the 727. The 737

horizontal stabilizer program includes graphite-epoxy skins and graphite laminate spars. Rudders and verticals are also being prepared under the NASA programs for the DC-10 and L1011.(14)

A most notable application of advanced composites to aircraft was the use of a graphite reinforced wing spar on the Gossamer Albatross. The Gossamer Albatross made history on 12 June 1979 when it became the first manpowered aircraft to cross the English Channel - a distance of 22 miles across water. It weighs 70 pounds, has a 96-foot wing span, and flies at an average speed of 11 miles per hour.

The key phrase of our national space effort from the beginning was "weight reduction." In an effort where it takes 20 pounds of fuel and engine to lift one pound of payload off the ground, weight savings must be a major consideration. Less weight translates directly into bigger payloads, longer range, or reduced fuel requirements. This concern for weight was a major factor in the development of the current miniaturized solid state electronics and a prime moving force in the development of composite materials. Initially, as with other industries, space applications utilized conventional materials and fiberglass reinforced plastics, but the need for greater improved weight reductions and performance has given momentum to the development and use of advanced fiber composites.

Some of the space vehicles and satellite applications include: rocket engine cases, pressure bottles, tanks, launch tube reinforcements, and air ducting. Advanced fibers used include graphite, Kevlar®, and boron, or combinations of fibers to form hybrid composites.

A major thrust for composite applications has been seen in NASA's space shuttle orbiter program. In all, thousands of pounds are used in its construction. A graphite-epoxy composite saves over 900 pounds in the 60-foot long by 15-foot wide payload bay doors. The titanium thrust structure is reinforced with 165 pounds of boron-epoxy composite. Graphite-epoxy is also used as reinforcement in the maneuvering system, and Kevlar®-epoxy overwraps reinforce metal pressure bottles.

Another major space application for composites is found in large space structures such as communication antennas. The requirement is for a light weight (for launch purposes), stiff structure with a high degree of thermal dimensional stability. Graphite composites which can be made with very low thermal expansion coefficients are well suited to these applications. One such current application is in the Intelstat V series of advanced communications satellites.

Consumer Goods--The uses of composites in the consumer goods industry include home furnishings (tables, chairs, beds), decorative accessories (lamp bases, flower pots, art objects), housewares, outdoor furniture and garden equipment, home power tools, sports equipment, and photographic equipment (camera and projector bodies). Composite use in consumer goods accounts for about six percent of all reinforced plastics and, with the exception of sports equipment, glass fiber reinforcements are used almost exclusively.

The use of advanced fibers (graphite, Kevlar®, and boron) in sports equipment was the first successful application of these fibers in the commercial sector. The products include tennis rackets, fishing rods, golf clubs, archery equipment, bicycle frames, hang gliders, ski poles, hockey sticks, surfboards, and helmets. The utilization of advanced fiber composites in sports equipment has been successful because of improved performance. Users claim that equipment made from these composites is lighter, better balanced, gives a better "feel" (stiffness, vibration damping) and has improved damage resistance. Because of this improved performance, the consumer and, especially, the experienced sportsman are willing to pay the cost premium for advanced fiber composite equipment.

Although the amount of fiber used in an individual item is not high, the volume is such that the sports equipment industry is a significant market for the fiber producers. The sporting goods market has, for the past five years, provided the graphite fiber manufacturers with the minimum

sales base which the industry has needed to survive. Sales have amounted to about 100,000 pounds per year, without which advanced fiber composites would be rarer and more expensive than they are now.⁽⁴⁾

Industrial--Industrial applications include construction, anticorrosion, electrical, and appliance uses. Some of the specific applications are listed below:

Construction - Bath fixtures (tubs, showers, and sinks), patio roofs, fences, garage doors, solar panels, signs, building supplies (cladding panels, doors, frames, pillars, roofs, ridge beams) concrete forms, ladders, materials handling equipment, pipe and tubing, storage buildings, ventilation (ducts, hoods, fans).

Anticorrosion - Chemical equipment, filter housings, fuel tanks, plating tanks, pump housings and impellers, tank cars, utility pole hardware, water mains, well casings, pressure bottles.

Electrical - Panels, switch gear, insulators, outlet boxes, transformer covers and pads, flywheels.

Appliance - Dishwasher parts, computer and typewriter housings, refrigerator cases, air conditioner housings, humidifier components.

As with commercial products most of the industrial composites utilize glass as the reinforcement fiber. As long as there is a significant price differential between glass and the advanced fibers, there will be little incentive to replace the glass. There are limited applications where advanced fibers have been applied because of superior performance. One of these is the use of Kevlar® in flywheels used as energy storage devices. Another is the use of Kevlar® in filament wound pressure bottles. Film cassette holders and patient support devices used in conjunction with

medical x-ray equipment are another recent application for Kevlar® and graphite. Composites are used because they have low adsorption of x-rays. Low x-ray absorption occurs because of the low density of graphite and Kevlar® fibers as well as the relatively low density of the resins systems used. The advanced composites provide excellent performance in areas where high structural integrity and stiffness are required to avoid deflection. The elementary truss structure as applied to crane booms and aerial ladders is another application of graphite reinforced plastics. The weight of the graphite can be as low as five percent of the weight of a comparable steel truss.

Commercial Applications - Metal, Carbon, and Ceramic Matrix Composites--

Applications for metal, carbon, and ceramic matrix composites are extremely limited outside of the military. The principal reason for this is cost. Another important factor is that the manufacturing technologies are in the early stages of development and are considerably behind the manufacturing technologies for plastic matrices.

Metal matrix composite processing techniques are well enough advanced for some of these materials (aluminum graphite, magnesium graphite, and aluminum boron), such that design data bases are sufficient for applications tradeoffs to be made with a fair degree of confidence. As with many other high-technology materials, much of the metal matrix composites developmental work has been government funded for military applications. A significant non-military application has resulted from work supported by NASA on the space shuttle orbiter program. Mid-fuselage frame tubes constructed from aluminum-boron composite play a major structural role in the orbiter spacecraft. These tubes have resulted in a 180-pound weight saving over conventional materials.⁽⁶⁾

The first significant commercial use of a metal matrix composite was an application in the "boron" tennis racket in 1975. A piece of boron reinforced aluminum was placed in the high-stress throat area of the racket. The result was increased racket stiffness and improved durability.

Approximately 1,000 pounds of aluminum-boron was produced in 1975 for this racket produced by AMF/Head, and this portion of the boron reinforced aluminum market exceeded the remainder of the military and aerospace markets combined.⁽¹⁰⁾

Some more recent applications for metal matrix composites are the use of graphite fiber reinforced copper for motor brushes and bearings. In the case of the brushes, the ability of the graphite to conduct electricity is a benefit. In both cases, the graphite adds strength, stiffness, and wear resistance to the components and is self-lubricating.

Carbon-carbon composite brakeshoes are in common use in military aircraft and are rapidly becoming accepted for commercial aircraft. Although the costs are high, they are very cost effective because they are lighter, more durable, and less trouble-prone than the conventional steel shoes. Currently, they are used on the Gulfstream III and Canadair Challenger business jets and on the Concorde commercial airliner. On the Canadair Challenger, the carbon-carbon brakes are 100 pounds lighter than comparable steel brakes and are good for a minimum of 1,600 landings compared vs. 600 for steel brakeshoes.⁽¹⁴⁾

Carbon-carbon composites have also been found to be useful in the medical field. Pyrolytic graphite is biocompatible with the human system for surgical implants. When strengthened with carbon fibers, the composite is being used for bone pins and heart valves. It also has potential application for total joint replacement, especially hip orthoplasty and dental implants.⁽⁴⁾

No current commercial applications for fiber reinforced ceramics were identified.

Military Applications--

Government funding has pioneered the use of advanced composites in many applications in the Army, Air Force, and Navy. Most of these applications involve the reinforcement of plastic matrices, but extensive past and current development activities with metal, carbon, and ceramic matrices have led to some current applications for these matrices. Fiber-glass reinforced plastics are still used in the military in applications somewhat parallel to commercial uses. There has been replacement of glass with advanced fibers, where the improved performance is merited, as well as new advanced composite applications, particularly where improved high-temperature performance is needed. Havard Wood of the Advanced Development Program Branch, Air Force Flight Dynamics Laboratory at Wright-Patterson Air Force Base stated: "Although there is some use of glass and aramids and occasionally boron, most of the current and near future composite components on military aircraft will be epoxy and graphite." (13)

The most significant uses of advanced composites are in the military aerospace applications in terms of numbers and quantities. Some of the principal applications to aircraft are shown in Table 3-7. There are other aircraft applications as well. The McDonnell Douglas AV-8B is the first aircraft designed with all composite wings. It has both main-wing skins and internal parts constructed with epoxy graphite, resulting in wings which are about 70 percent composite by weight and make up about 22 percent of the total aircraft weight. The production model of this aircraft will also have forward fuselage and the horizontal stabilizer constructed from graphite reinforced epoxy, resulting in an aircraft with advanced composites that account for about 29 percent of its weight. (18) Other applications for advanced composites include: epoxy-boron wing tracking edge panel in F-111, epoxy-boron leading edge slat in C-5A, epoxy-graphite underwing fairing in F-111, and epoxy-boron rudder in F-4.

TABLE 3-7*
ADVANCED COMPOSITES APPLICATIONS IN
MILITARY AIRCRAFT CURRENTLY IN PRODUCTION

Plane	Material	Component	Advanced Composites Utilization	
			Weight per Aircraft lbs (kg)	Weight Percent of Aircraft Structural Weight
F-14	Boron Epoxy	Horizontal stabilizer	186 (85)	0.8%
F-15	Boron-Epoxy Graphite Epoxy	Empennage Speedbrake fins	215 (98)	1.6%
F-16	Graphite Epoxy	Empennage fin covers	180 (82)	2.5%
F-18**	Graphite Epoxy	Upper and lower wing skins, horizontal surfaces, speed brake panel, fuselage ventral section, leading edge extension, landing gear doors	1,100 (500)	9.5%

* Reference 4.

** Pre-production.

There has been extensive development work to utilize composites in aircraft engines. Organic resin composites can be used in the cooler regions of an engine, but extensive use of composites would require the improved high temperature performance provided by metal and carbon matrices. There are several problems which must be overcome before advanced composites can be used in engine applications. Current foreign object damage, reliability, and quality control. One of the major development efforts are concentrating on aluminum Borsic® or boron fan blades and vanes and titanium Borsic® or boron carbide coated boron fan blades, vanes, and shafts. Du Pont's NR-150 polyimide reinforced with graphite is currently being tested for use as divergent exhaust nozzle flaps on the Pratt and Whitney F-100 engine. The composite flaps have successfully withstood over 100 hours of testing. They also have withstood over 600°F during flight testing on a F-14.

Carbon-carbon composites are being used at the rate of about 10,000 pounds per month for military aircraft brakeshoes. Development efforts to apply carbon-carbon composites to the divergent flaps on the F-100 engine exhaust section are well advanced.(19)

Composites have been used extensively in helicopter rotor blades. Initially, fiberglass composites were used to replace metal. Currently most blades are fabricated with glass graphite or glass Kevlar® hybrid composites. Such blades are currently in use in the Army UH-60A Blackhawk and the CH-46 main rotor blades. Other composite uses in helicopters have included reinforcement of the aluminum stringers on the tail cone of the Sikorsky/U.S. Army CH-54 with unidirectional boron-epoxy strips and reinforcement of the tail skid with boron epoxy. Current versions of the UH-60A and SH-60B helicopters for the Army and Navy, respectively, utilize about 150 pounds of epoxy Kevlar® for secondary structural elements.(4)

Engine and transmission vibration noise has been reduced on the CH-47 helicopter by bonding an aluminum graphite composite doubler plate to critical areas of the transmission housing. Kevlar® reinforced polyester seat buckets are being used in helicopters as armor to protect personnel from small arms ground fire.

The requirements for high performance and light weight have made advanced composite applications a natural for missiles, rockets, and satellites. Composite use in spacecraft includes engine casings, rocket bodies, fins, nose cone, re-entry shields, structural elements, rocket nozzles, antenna systems, fuel tanks, and pressure bottles. In the early days of rocketry, fiberglass reinforced plastics were used for many of these applications when temperatures permitted. The current advanced fibers now make possible high temperature applications and have replaced glass in many of the low temperature applications. A good example of the use of composites is the Trident (C-4) ICBM which uses graphite and Kelvar® to improve range and performance. Applications include: an epoxy-graphite critical equipment section structure, graphite composite post openings for nozzle and igniter assembly as well as the rocket nozzles. The missile cases are constructed from epoxy-Kevlar® and achieve a 25 percent weight reduction over fiberglass reinforced plastic.

Graphite reinforced epoxy is an excellent material for communications satellites because of its high strength, high stiffness, and thermal stability (low coefficient of thermal expansion). It also can be made to be electrically conductive. Kevlar® reinforced epoxy is commonly used in applications requiring low thermal conductivity in addition to high strength. Military applications for composite materials other than aerospace include: launch tubes; bridge and craft trusses and beams; boat hulls; vehicle bodies, frames and drive shafts; and sewage, water and petroleum pipes. The Navy is currently funding efforts to construct small high-speed boats using Kevlar® reinforced polyester. Advanced composite hydrofoil craft are also being developed.

Current Materials Costs and Production Quantities

Current estimates of costs and production quantities obtained from various references are given in Tables 3-8 and 3-9 for fibers and composites, respectively.

TABLE 3-8
PRODUCTION AND COST OF COMMERCIAL REINFORCEMENT FIBERS

	<u>Production, 1,000 lb/yr</u>	<u>Cost, \$/lb</u>	<u>Source</u>	<u>Reference</u>
Alumina FP	Experimental	200	DuPont	(6) (4)
Boron	40-50 all boron forms (1980)	200-500	Avco, Composite Technology, Inc.	Avco
Glass	860,000 (1979)	0.58-0.81	Owens-Corning, FRg, Certain Teed, Reichold	(23)
S-glass		2.50		(20)
Graphite	1,000 all graphite forms (1980)		Avco; Celanese Advanced Composites; Great Lakes Carbon Corp.; Hercules, Inc.; Morganite Modmore, Inc.; Stackpole Fibers Co.; Union Carbide Corp.;	UC
PAN 3000 Filament		30		UC
PAN 6000 Filament		21		UC
PAN 15,000 Filament		18		UC
PAN Very High Modulus Pitch		100-200		(4)
		20		UC
Kevlar®	1,200 (1979)	8-27	DuPont	(4)
Silicon Carbide	0.2	390	Avco, FMI	Avco
SIC Whiskers	2	95	Exxon Enterprises	Exxon
All Reinforcements	1,131,000			(20)

TABLE 3-9
COMPOSITES PRODUCTION QUANTITIES AND COSTS

<u>Composites</u>	<u>Production, 1,000 lb/yr</u>	<u>Cost, \$/lb</u>	<u>Reference</u>
Plastic-glass	2,200,000 (1980)		(20)
Plastic-graphite	2,000 (1980)		(20)
Plastic-hybrid	1,400 (1980)		(20)
All	2,204,000 (1980)		(20)
Reinforced Polyester	1,756,000 (1979)	0.74-0.88 (1978)	(21) (2) costs
Reinforced Epoxy	53,000 (1979)		(21) (2) costs
Glass/graphite		2.88 (1978)	(4)
polyester hybrid			
Aluminum-boron preform	1 (1978)	250-300 (1978)	(4)
Aluminum-boron		350-400 (1978)	(4)
Aluminum-graphite	0.5-1 (1978)	300-400 (1978)	(4)
preform			
Aluminum-graphite		700-900 (1978)	(4)
Epoxy-graphite prepreg	(1978)	40-60 (1978)	(4)
(high strength)			
Epoxy-graphite prepreg		180-200 (1978)	(4)
(ultra-high modulus)			
Epoxy-boron prepreg		190-200 (1978)	(4)
Epoxy-Kevlar® prepreg		30 (1978)	(4)
<u>Nonreinforced Resins</u>			
Polyester		0.52 (1980)	(22)
Polyester thermoplastic		0.60-1.20 (1980)	(22)
Nylon 6/6		1.34 (1980)	(22)
Polyimide		up to 100 (1978)	(4)
Epoxy		0.70-10 (1978)	(4)

SECTION 4

TRENDS

INTRODUCTION

According to The Society of the Plastic Industry, Inc. (SPI) Conference News released at the 36th Annual Reinforced Plastics/Composites Conference on February 18, 1981, shipment of reinforced plastics composites in 1980 were off 18 percent to an estimated 1.68 billion pounds, but the industry anticipates an 11 percent rebound in 1981 to a projected volume of 1.87 billion pounds.(23)

In May, 1979, Modern Plastics Magazine stated that the importance of the role that the advanced fiber composites composed of graphite, Kevlar®, and hybrids with glass will play in plastics product design and manufacture during the next decade can best be appreciated by these numbers: 250,000 tons is the estimated sales volume for 1990, the same amount processed by the entire glass-reinforced plastics industry for all applications in 1965.(19)

Materials Engineering Magazine indicated in January, 1980, that even the so-called exotic composites are finding their way into relatively ordinary applications. Carbon/carbon composites developed for unique aerospace applications, such as rocket nozzles for the MX missile, the Space Shuttle's In Upper Stage (IUS), and for nosetips for the new generation of re-entry vehicles, are now being used for brakes on commercial aircraft and for jet engine nozzle flaps on the F-100 engine. Metal-matrix composites are finding their way into advanced jet engine designs, tank tracks, bridges, etc.(24)

In spite of rose-colored predictions that can be traced back several years, the reinforced plastics market lost ground in 1980. Gigantic inroads were not made into the automotive industry as predicted in 1979 for a number of reasons. Short-term impacts on the market growth were affected by the disastrous decline of the boat industry, showing a composites usage decline of 28.5 percent to 275 million pounds against 1979 sales. This was the worst year in two decades for the boat industry. The land transportation industry, largest user of reinforced plastics, cut purchases in 1980 by 20.6 percent. The RP/C industry slid from its all-time high of 2,059 billion pounds in 1979.⁽²⁵⁾ It should be noted that RP/C's figures include a far broader range of composites than just advanced composites, but the trends are the same.

There are a number of long-range impacts on market growth that can be traced to recent decisions made by industries, such as the automotive industry on the direction of their engineering advances because of the nature of this material. Technologically, it is possible to make practically the entire automobile out of various types of plastics. This will not happen for some time due to competition from other materials, the requirement for extensive capital investment, and production speed. Detroit has decided to meet U.S. Environmental Protection Agency mileage standards by downsizing. The 1985 Corporate Average Fuel Economy (CAFE) requirement is one formidable barrier to the growth of automotive plastic composites. For example, a company with a 1977 CAFE of 18 mpg must gain 9.5 mpg by 1985. Eight hundred pounds of weight loss alone would provide an increase of 4.0 mpg. Drive train improvements could result in an increase of 5.2 mpg, advanced aerodynamics and tire design will provide an increase of 1.5 mpg. This amounts to a total increase of 1.2 mpg beyond the 1985 CAFE goal without adding a single ounce of composites.⁽²⁶⁾

Detroit's inherent bias toward metals represents still another obstacle in the way of composite materials market growth. The billions of

dollars invested by the Big Four, mostly in the past five years, in metal-working tools will not be amortized for several more years. They will also spend about \$85 billion to meet 1985 CAFE requirements. In conjunction with the dramatic sales slump affecting the industry presently, it is unlikely that anyone is anxious to reinvest in capital equipment for plastics.

The problem is compounded by the fact that composites fabrication falls substantially behind steel and aluminum. Present captive and custom operations cannot realistically supply parts for production runs greater than 250,000.⁽²³⁾ This is a small number in light of the fact that 8.3 million cars were domestically produced in 1979 and 9.8 million are projected for 1984.⁽⁶⁾ To overcome low productivity, prohibitively large capital investment is needed. Converting a door or a deck lid on one car line to a sheet molding compound (SMC) requires the purchase of as many as thirty 2,000-ton hydraulic presses at about \$1 million each, more capacity than any U.S. facility has in existence. Processing speed represents another obstacle to converting to composite materials. In the short run for quick fixes such as skimming a few pounds to drop weight-inertia classes, engineers will choose aluminum even if it is more expensive. Aluminum saves design, engineering, and manpower time and can meet production schedules, and redesign is less costly.

New grades of high-strength steel with improved formability and lighter weight offer even stiffer competition to composites. For example, Ford designed a glass-fiber reinforced composite to replace 35-pound steel transmission supports. A 27-pound weight savings could be realized. However, by the time the piece was developed and tested, the original support had been redesigned into a tubular high-strength steel configuration weighing only 12 pounds.

Dramatically improved corrosion resistance of galvanized steel has further slowed the rush to composites. If cars were rusting at rates common ten years ago, consumers and the federal government would demand composites, but new grades of steel and coatings are stable enough for the industry to offer no-rust warranties.⁽²⁷⁾

Additional hindrances to the growth of composites usage in the automotive industry include:

- Plastics price increases will most likely surpass inflation due to surging oil and energy prices and to chemical companies' anticipations of cost increases to ensure funds for research and development.
- Detroit expects a slowed growth and ultimate plateau of car sales by the mid-decade. This is tied to increased car life and to demographic trends which show a decrease in the growth rate of individuals in younger age groups.
- Public perception of plastics as being "cheap" lingers on. This concern is slowing introduction of both plastic wheels and fuel tanks. Manufacturers will introduce plastic wheels as spares around 1983 and add the other four tires only after a period of acceptance.
- Safety factors related to public perception and federal government regulations present another barrier. In general, metals continuously absorb energy as they collapse, while plastics shatter or, at best, tear.

The preceding paragraphs paint a dismal picture of the future of composites especially in the automotive industry. However, the bottom line for the future of composites is one of clear growth, although not the exaggerated growth previously predicted. In spite of the slide of the composites industry in 1980, a continuing stream of new applications for these strong, lightweight, corrosion-resistant, energy-efficient materials cushioned the fall, and the decline was consistently less than those recorded by the industries served. In the aircraft and aerospace and corrosion-resistant equipment market, 1980 poundage shipments of reinforced plastics were up by 8.7 percent and 4.6 percent, respectively.⁽²⁵⁾ This enthusiasm and optimism were reflected in the fact that attendance reached 2,083 at the 36th Annual Reinforced Plastics/Composites Conference, February 16-

20, 1981. A record number of hospitality suites were reserved, and the number of exhibits surpassed all past records.

In the auto industry, financial problems, decreased productivity, and downsizing will only slow, not stop the use of composites in automotive applications. Composites must be exploited on low production runs. For example, a vented hood will be featured on Chevrolet's 1981 Citation sports model. Tooling costs for a production run of this size, less than 30,000 units, for SMC molds are far less costly than tooling for stamping steel or aluminum. Composites have an advantage over metals in tooling costs on production runs up to 100,000 units.⁽²⁶⁾ Limited revenues will result in a cutback in the number of car models. The public will still demand a variety of products; therefore, designers will take existing car lines and add hoods with composite air scoops, spoilers, reinforced-reaction-injection molded (RRIM) polyurethane fenders, etc. This philosophy justified the use of RRIM fenders on the 10,000 unit Sports Omega, but not on the 300,000 unit standard model. This was due to the fact that 500 steel fenders can be stamped out per hour versus molding only 20 to 30 composite fenders in the same period. It is also projected that designers will decide to develop large cars that weigh the same as downsized cars in the future. This can only be done with composites.

The electric car will serve as a boon to the composites industry. General Motors has already committed itself to introducing an electric vehicle by 1985. The electric car and the forthcoming two-passenger commuter car will require lightweight, high-strength materials, and both cars represent low-volume production which is ideally suited to the use of composite materials.

The future of composite materials will be one of growth although not as dramatic a growth as predicted in the past. The remainder of this section will describe the future trends of various technologies and activities directed at overcoming obstacles to growth that were alluded to above. Key economic factors that could change the course of the future of composites future trends for various classes of composites are also discussed.

MANUFACTURING TECHNOLOGY

State-of-the-art manufacturing processes are described in Section 3. As indicated in the introduction to this section, significant progress is necessary if the area of impact of composite materials is to be broadened to include such industries as the automotive industry. Progress is being made under the auspices of federal government manufacturing technology programs and industrially funded research and development programs.

In recent testimony before the Defense Industrial Base Panel on the House of Representatives Committee on Armed Services, William J. Perry, Undersecretary of Defense for Research and Engineering, stated that the DOD Manufacturing Technology Program is clearly an extremely important vehicle for improving the health of industry and addresses improving the productivity and responsiveness of the industrial base by developing advanced manufacturing techniques, processes, materials, and equipment.(28) Manufacturing technology programs funded by all three military services are presently advancing the state of composites manufacturing. The resultant defense related applications will have dramatic impacts on composite usage in commercial applications.

Grumman Aerospace has broken down the cost of composite manufacture as shown in Figure 4-1.(29) They are using their first generation automated equipment, the Integrated Laminating Center (ILC) for F-14 aircraft stabilizer production. The ILC automates tapelaying or broad goods dispensing, nesting and trimming, inspection and ply-handling, and stacking operations. The ILC is the core of Grumman's newest system, Advanced Integrated Manufacturing System (AIMS), which is under development for production rate fabrication of large, complex-curvature hardware. Eventually, AIMS could have parallel laminating centers and banks of autoclaves. The accuracy of various manipulators are presently being investigated. The accuracy of commercially available robotic manufacturing equipment is the principal area of concern.

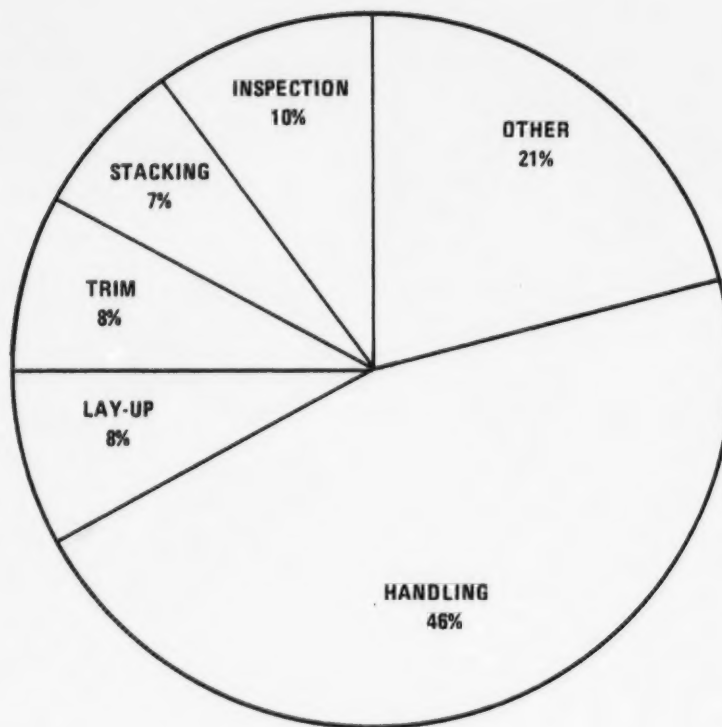


**FIGURE 4-1. GRUMMAN AEROSPACE AIRCRAFT COMPOSITE
MANUFACTURING COSTS^{2 9}**

Northrop's futuristic composite fabrication facility will feature automatic dispensing, a Gerber cutter (a programmed, automatic machine to cut plies), an electrified overhead monorail system, robots for ply transfer and stacking, a scrap-removal system to scrape off trim, and an automated inspection system. They will rely heavily on robotics. Automated resin curing systems are also under development. Based on resin resistance change measurements, a computer will dictate required time-temperature profiles.(29)

Under Air Force contract, Northrop is automating the cleanroom, project Integrated Flexible Automation Center (IFAC). Automated video inspection is a major attribute of IFAC. Video information is picked up and converted to digital information, the basis of which is a "blue box." The box was developed for smart weapon systems that look through trees in search of tanks. It is now being modified by Northrop to control quality of the intermediate material of the prepreg. The system looks for voids, open weaves, and checks fiber alignment. The Gerber cutter can then be told that there is a soft spot ten feet into the fabric and it will cut around it. In the future, Northrop sees no requirement for expensive autoclaves, but will use a vacuum-bag cure. They are also looking at automating autoclave curing and loading, tools, layup, and bonding. As for automated assembly, a two-armed robot is on order. It will pick up a graphite component such as a horizontal stabilizer, move it to an assembly line, and position it to within ± 0.010 inches.(29)

The above referenced manufacturing technology represents only a portion of that funded by the federal government. Most of this effort is aimed toward aerospace applications, but it impacts commercial applications for composites through the trickle-down effect. Industry is not standing by waiting for the trickle, rather it is executing a substantial effort of its own to bring the cost of composites in line with their needs and requirements.

There are several key materials technology problems that stand between the present small-scale application of composites to automobiles and widespread composite autos. They include the following: long production times, waviness and porosity, temperature limitation (e.g., painting), and insufficient stiffness in state-of-the-art chopped fiber reinforced composites.⁽³⁰⁾ In response, Detroit is investigating a wide range of new processes and manufacturing methods. In addition to faster Sheet Molding Compounds (SMC) processes and processing, automation for RIM is being studied. Hybrid SMC's, pulmolding, pulforming, automated filament winding, elastic-reservoir molding (ERM), and plastic-metal laminates are being explored.

Table 4-1 outlines predictions on the future of composites manufacture for automobiles according to officials of General Motors. The impact of these processes was assessed in a Delphi forecast conducted by Arthur Anderson and Company along with consultants from the University of Michigan entitled, U.S. Automotive Industry Trends for the 1980's. Figures 4-2 and 4-3 show a clear shift away from steel to plastics and aluminum. Figure 4-4 ties this shift to projected body weights for present and future vehicles. The usage of polymer-based composites is expected to grow from 35 pounds per car in 1980 to 100 pounds by 1985, and to 200 pounds by 1990. Fiber reinforced plastics will be specified for more exterior panels. It is predicted that in 1985, 10 percent of these panels will be composites and this will double by 1990.⁽³¹⁾

Advances in manufacturing technology on all levels from fiber production to composite production will drive the price of the finished part down. For example, it is predicted that graphite composite costs, presently \$20 per pound, will fall to \$15 per pound in 1985 and \$10 per pound in 1990 (based on 1979 dollars).⁽³¹⁾ This fact coupled with the increased value of shedding pounds will drive Detroit to composites. Table 4-2 depicts the growing value of lost weight according to predictions made by various segments of the auto industry.

TABLE 4-1. BODY PANEL, STRUCTURAL COMPONENT PROCESSES⁽³⁰⁾

<u>Projected Date of Introduction</u>	<u>Process</u>
Short term	● Reaction injection molding, reinforced reaction injection molding, sheet molding compound
Mid-1980's	● Compression molding of hybrid SMC: chopped/continuous fiber reinforced ● Reaction injection molding with inserts, tubular metal and disposable foam cores
1990	● Reaction injection molding of epoxies, nylons, and polyesters ● Pulforming, pulmolding ● Filament winding ● Automated postmolding operations
No Major 1980's usage	● Blow molding ● Stamping ● Structural foam ● Injection molding

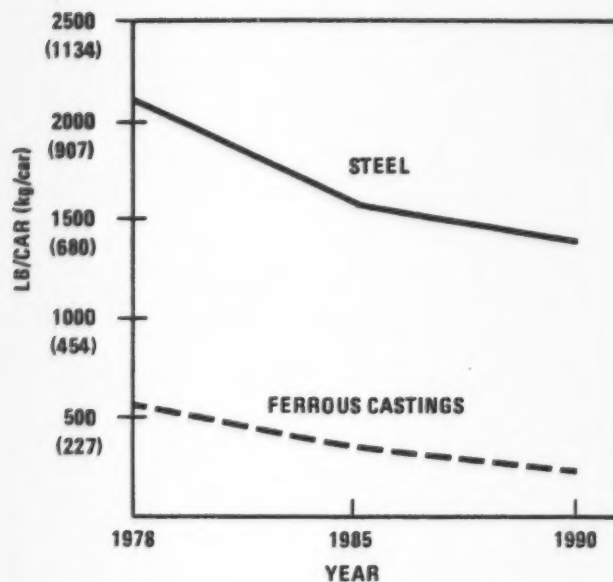


FIGURE 4-2. PROJECTED USE OF STEEL AND IRON IN U.S. PRODUCED CARS (SOURCE: ARTHUR E. ANDERSON & CO.)⁸⁸

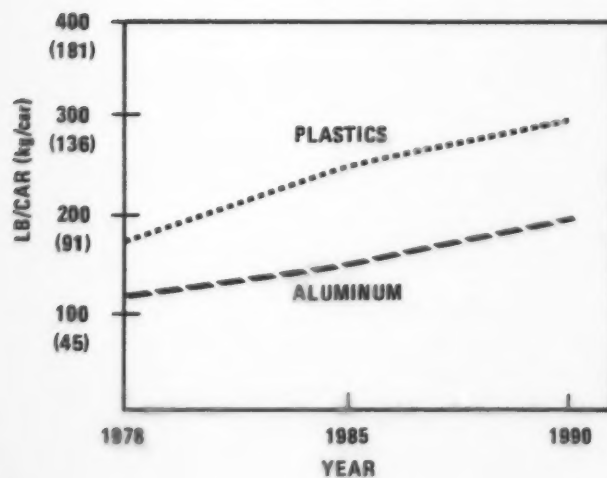
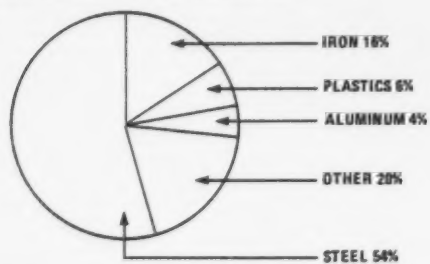
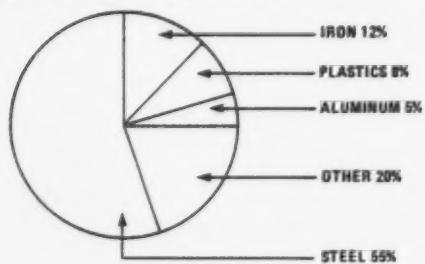


FIGURE 4-3. PROJECTED USE OF LIGHTWEIGHT MATERIALS IN U.S. PRODUCED CARS (SOURCE: ARTHUR E. ANDERSON & CO.)⁸⁸

AVERAGE 1980 CAR WEIGHT 3300 LB (1500 kg)



AVERAGE 1995 CAR WEIGHT 2900 LB (1320 kg)



AVERAGE 1990 CAR WEIGHT 2500 LB (1130 kg)

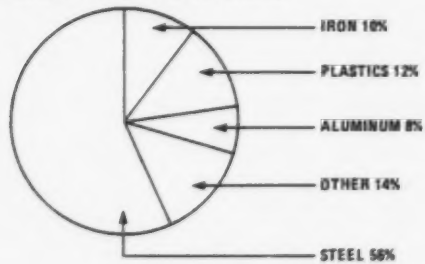


FIGURE 44. FUTURE USE OF MATERIALS IN U.S. PRODUCED CARS
(SOURCE: ARTHUR E. ANDERSON & CO.) ^{6 8}

As a final illustration of the direct impact of manufacturing technology on the economic elements of composite parts, Owens-Corning engineers used the Chevrolet Citation hood to present three techno-economic analyses of what advances in SMC processing that are now under intensive study will bring by 1982 (Table 4-3). By 1982 the SMC hood is seen as being competitive for volumes up to 350,000 units annually, in comparison to the present 225,000 unit breakeven point.⁽³²⁾

Quality Control and Product Reliability

Product reliability is essential to market growth. The product must provide long trouble-free life under expected loading and environment conditions. The ultimate user must be assured that the ultimate strength, load limit, fatigue characteristics, and residual strength of these materials during the operational life of the structure are well defined and well understood. A new structural technology must not present any reliability or maintenance surprises. Such surprises can lead to major market setbacks. The introduction of composite wheels for automobiles will be done slowly to assure the public of their viability. With the natural skepticism the public holds toward plastics, high quality and reliability are even more important than that required of metals. It should be noted that this skepticism resides in the minds of many design engineers who have become comfortable with the metals that are to be replaced or displaced through experience.

Engineers and scientists are spending a significant fraction of past and present efforts in advanced composite development. They are obtaining a better understanding of basic composite materials properties, developing test methods, acquiring a statistically significant experimental data base needed to establish safe, reasonable material allowables, determining the effects of long-term environmental exposure, and developing accurate design procedures and methods of structural analysis which take into account the non-isotropic properties of advanced composites.

TABLE 4-2. VALUE OF FUTURE WEIGHT SAVINGS AS PREDICTED
BY VARIOUS SEGMENTS OF THE AUTO INDUSTRY (\$/lb)⁽³¹⁾

<u>Segments</u>	<u>1979</u>	<u>1985</u>	<u>1990</u>
Research	0.90	1.00	1.25
Manufacturers	0.50	1.00	1.13
Suppliers	0.50	1.00	1.50

TABLE 4-3. MAJOR MANUFACTURING ECONOMIC ELEMENTS FOR FINISHED
CHEVROLET CITATION HOODS

	Current			Projected
	<u>Steel</u>	<u>Aluminum</u>	<u>SMC*</u>	<u>SMC*</u>
Total Hood Weight (lbs)	34.94	23.87	23.05	23.05
Material Weight (lbs)	32.87	21.80	22.00	22.00
Material (\$/hood)	12.36	29.75	14.53	14.05
Cycle Time (sec)	8	8	180	120
Total Output (units/hr)	300	270	16.5	25.8
Labor (\$/hood)	1.05	1.17	3.20	1.59
Tooling (\$/hood)	10.00	10.00	3.20	1.75
Total Tooling Expenses (\$ millions)	4.0	4.0	1.15	0.7

* SMC - Sheet Molding Compound

Historically, the growth of advanced composite materials has been characterized by significant conservatism and restraint. Products are generally overdesigned and the time from laboratory to the field has been extremely long. Composite materials in the lab now are not likely to be in widespread service until after the year 2000.⁽³³⁾ With few exceptions, extensive testing and analysis have been performed before the incorporation of a composite in an operational aerospace or automotive application. As in the case of automotive parts, small parts are used first and extensively field tested before any full-fledged structural components see action. To date composites have almost exclusively been used on a substitute basis. The replaced metal part is held back as a replacement in case the composite does not live up to expectations. Only now, after over 15 years of experience, are composites being looked at seriously as in the case of the Ford all-graphite car, the new Lear Fan business aircraft, and the Windecker Eagle which is the first all-composite aircraft certified by the FAA to use fiberglass/epoxy for the primary airframe.

This approach has resulted in a slow but steady evolution of advanced composite technology, marred by a few accidents and surprises (e.g., the destruction of graphite/polysulfone composite spoilers by aircraft hydraulic fluids).⁽³⁴⁾ This approach demands patience and a large budget. It has constrained the development and introduction of new technology. The certification cycle required to qualify a raw material or manufacturing process tends to promote continued use of tried and proven materials rather than the introduction of new materials with the promise of improved performance.

New nondestructive testing (NDT) methods, design technology, and better coordinated composite materials data banks are making the efficient safe usage of composites a reality. In-process inspection techniques such as the Northrop automatic video inspection system,⁽²⁹⁾ improved acoustic emission testing for final inspection prior to being placed in service,⁽³⁵⁾ and ultrasonic flaw detection to locate disbonds and delaminations in composite laminates and joints will lead to greatly enhanced

confidence in composite materials.⁽³⁶⁾ In-field NDT will also increase confidence and build up a life cycle data base that can be applied in the future. This process is self-reinforcing. As more experience is gained with a given material and manufacturing method, a greater level of confidence will be obtained in that material and/or method and the greater the probability it will be re-specified. At the same time, the data base will allow for a better understanding of the properties of the material and a better ability to design safe, efficient structures. This will lead to the introduction of a composite to new markets, where its full potential can be utilized and the economics of introducing it are more favorable. Together these factors further enhance the likelihood of the widespread future use of composites.

As a technology matures, new problems arise and are solved. For example, the National Bureau of Standards (NBS) stated: "A significant detriment to the expanded use of composite materials in all areas of consumer technology is seen to be the difficulty of associating performance with the profusion of products identified by trade names. Composite technology would greatly benefit from the establishment of an industrial standards group which would establish a numerical composite classification system based on key elements affecting performance." NBS has proposed a system in which mechanical, electrical, and thermal properties are defined by a number-letter combination defining type and flexibility of the matrix, the type and configuration of the reinforcement, and the reinforcement volume fraction. American Iron and Steel Industries designations for Steel and Aluminum Association designations for aluminum alloys serve as models.

TYPES AND QUANTITIES OF ADVANCED FIBER COMPOSITES

Advanced fiber-reinforced composites are a rapidly maturing new class of materials. The ability to tailor-make composite materials and structures offers opportunities for a broad spectrum of military, space,

and industrial applications. This section will project future applications for various categories of advanced composites. These projections are based on open literature, interviews of key members of the advanced composites community, and the aggregate experience of Versar's staff. The major categories to be discussed are segregated by matrix material.

Plastic Matrix Composites

Fiber-reinforced polymer producers suffered through 1980. Prospects for 1981, although improved, put reinforced polymers shipments in the United States back to just a little above 1977 levels. The two billion pound shipments mark, reached in 1978, will not be reached again until at least 1982. It should be noted that these shipment figures apply to all polymer composites and not just the advanced fiber composite subset, but the trends illustrated apply to both markets.

The 1980 drop of 18 percent to 1.685 billion pounds (Table 4-4) was buffered by new applications. Because of the new uses, the declines were consistently less than those recorded by the industries that make up the end-use markets. The prospects for 1981, although an improvement from 1980, will put reinforced plastics shipments in the United States back to just a little more than 1977 levels, or to a projected level of 1.871 million pounds.

The biggest drop in shipments in 1980 was for reinforced plastics destined for marine use (mainly hulls for pleasure and commercial boats). Marine use fell 28.6 percent in 1980 to 275 million pounds, and shipments to the marine industry have dropped 36 percent from their all-time high of 430 million pounds in 1978. In a slow economy big-ticket, durable goods such as pleasure boats normally suffer. The land transportation industry, also hit by recession, dropped by 20.7 percent in 1979 to 436 million pounds.⁽³⁷⁾ A general increase of 11 percent is projected for 1981, with gains projected in all industries. These projections are depicted in Table 4-4.

TABLE 4-4
REINFORCED PLASTICS DEMAND³⁷

Millions of lb	1981	1980	1979	1978	1977	1976	1971	Percent Change		Percent Average Annual Change
								1980-81	1979-80	1976-81 1971-81
Transportation, land	474	436	550	535	475	398	195	8.7	-20.7	3.6 9.2
Marine	325	275	365	430	400	365	267	18.2	-28.6	-2.3 2.0
Construction	309	265	335	320	286	248	152	16.6	-20.9	4.5 7.4
Anticorrosion	261	249	238	216	192	157	92	4.8	4.6	10.7 11.0
Electrical	178	162	190	170	147	123	53	9.9	-14.7	7.7 12.8
Appliance	112	104	130	123	112	98	47	7.7	-20.0	2.7 9.1
Consumer goods	110	99	126	116	107	102	74	11.1	-21.4	1.5 4.0
Aircraft	28	25	23	22	21	22	23	12.0	8.7	2.6 2.0
Other	74	70	79	74	70	66	69	5.7	-11.4	2.3 0.7
TOTAL	1,871	1,685	2,056	2,006	1,810	1,579	972	11.0	-18.0	3.4 6.8

By far the largest portion of the reinforced plastics market is made up by reinforced polyesters. The 1980 polyester market was off by as much as 25 percent from 1979. The projected outlook for 1986 is for a steep ascension following 20 years of more gradual growth (from 1,183 million pounds in 1979 to a level of 1,952 million pounds in 1986)(38).

Assuming that the remainder of the reinforced plastics market is fixed (highly unlikely), the reinforced plastics market will reach a level of 2,829 million pounds, or an increase of 51 percent. On a market-by-market analysis, it is apparent that the major area of growth in reinforced plastics will be in the land transportation market, primarily automobiles. This market alone should grow by 183 percent in polyesters by 1986.

The overall plastics industry is projected to undergo significant growth in the next 20 years, with consumption climbing from the 1970 level of 16.7 billion pounds to 227 billion pounds in the year 2000, representing a growth rate of 8.6 percent per year. A similar growth rate in the reinforced plastics portion of the market would indicate that the year 2000 market would be 6.196 billion pounds. Based on historical growth data (1980-81 percent change of +11.0 percent, and a 1971-1981 percent annual growth of 6.8 percent), this number is more likely conservative.

Plastics production is one of the fastest growing segments of the rapidly expanding chemical industry. It is expected to contribute about 7.2 percent to the Gross National Product, based on plastics fabrication projected for the year 2000. It will employ about 1.3 percent of the labor force. These figures represent a significant increase from the present 1.9 percent of the GNP and one percent of the labor force.

Several factors can significantly alter the projections for the year 2000. The most important ones are:(39)

- Availability of petrochemical feedstocks.
- Insufficient research and development to increase productivity and maintain strong domestic and international competition.
- Major disruption of domestic economic activity because of unforeseen world political changes.

The factors would have to be altered to fit the reinforced plastics market. For example, insufficient petrochemical feedstocks would be tied to high gasoline prices, which would push the automakers and aircraft industry towards greatly increased usage of lightweight energy efficient reinforced plastics. This increase in market share would be partially offset by a reduction in marine markets, inspired by reduced pleasure boat usage and purchase, but it should override the general effect. The general trend toward increased energy costs will accelerate the advent of widespread usage of structural composites, probably at a growth rate faster than the overall plastics industry. Basically, it is difficult to make an accurate prediction of the size of the reinforced plastics market as in the year 2000 as evidenced by the unforeseen dramatic drop in the 1980 market and the decision by Detroit to downsize rather than "plasticize" its fleet until 1985. A steady growth projection is highly probable and an 8.6 percent annual rate is within reason.

The future of plastic matrix composites will be investigated by first categorizing the applications by reinforcement fiber, then by type of matrix. This description is given below.

Fiberglass-Reinforced Composites--

Fiberglass is, by far, the most widely used reinforcing fiber for composite materials. This study only looked at E and S grades or better grades of glass. The present applications for these materials are covered in Section 3. As mentioned in the Introduction (Section 2), glass fiber reinforced composites are the pioneer materials of the composites industry. The applications, present and future, for glass composites may eventually be applications for advanced composites. The technologies developed for the fabrication of glass fiber reinforced composites are generally universal technologies that are directly applicable to advanced fiber composite fibers such as graphite or Kevlar®. It is, therefore, essential to investigate and analyze the future of glass composites if one is to predict the future of advanced composites accurately.

Fiberglass reinforced plastics include a multitude of materials from polyesters to epoxies to vinyl esters. In the course of this study, 15 plastic matrix systems were investigated. Some of these, like unsaturated polyester, see widespread use in composites and are covered in great detail; others are either totally devoid of composite applications or see insignificant usage as composite matrices. Some exotic systems may have been overlooked, while others will undoubtedly be discovered in the 1981-2000 time frame covered in this study. But it is certain that systems not presently in widespread use, at least with glass fibers, will not be in significant usage by the year 2000. The gestation period for a composite is extremely long since it generally replaces other systems such as metals, which are well characterized and have instilled in them a great faith in their utility.

Glass Reinforced Thermoplastics-- Highly reinforced thermoplastics are growing rapidly in use both in the United States and in Europe. Glass fiber reinforced thermoplastics offer high tensile strength, high flexural modulus, and low creep, and they can be readily molded on injection equipment. Normal fiber loadings range from 40 percent to 60 percent.

Presently, the European automotive industry uses one-half million pounds of 50 percent glass reinforced nylon 6, and this usage is growing. This trend toward glass reinforced thermoplastics is also growing in the United States. Reinforced nylon is found in automotive, photographic, appliance, recreational, military, business-machine, electronics, and chemical processing applications. Resin systems involved include polycarbonate super-tough nylon, thermoplastic polyester, polyphenylene sulfide, polypropylene, acrylonitril butadiene styrene (ABS), styrene-acrylonitrile (SAN), polystyrene, polyethylene, polysulfone, polyacetal, thermoplastic polyurethane, and modified PPO.

High tensile strength and short-term heat resistance make reinforced thermoplastics attractive to many materials designers. Cost is also an extremely important factor. This is especially true in the choice of the

reinforcing member. For example, when investigating performance per unit cost, while glass reinforced polypropylene ranks low in the basic properties ratings and carbon fiber reinforced nylon 6/6 ranks much higher, but glass-polypropylene could be a far better selection in an application (especially when impact is important) and costs are considered. Conversely, where rigidity is critical carbon/nylon may be the best choice despite the high cost. Finally, the ability to injection mold these glass reinforced plastics increases their attractiveness even further.⁽⁴⁰⁾

Glass Reinforced Thermosets-- By far the largest volume of glass fiber reinforced plastic is in the form of glass reinforced unsaturated polyester. These products offer an attractive balance of low cost and good mechanical, electrical, and chemical properties as well as ease of handling. As covered in Section 3, polyester composites are fabricated by hand layup, sprayup, filament winding, pultrusion, compression molding of sheet-molding compound (SMC), bulk molding compound (BMC), thick molding compound (TMC). Polyester composites reinforced with glass cut across the entire spectrum of applications for glass composites: marine, land transportation, aerospace, construction, anticorrosion, electrical, appliance, and general consumer goods. The greatest promise for future applications of this material lies in automotive applications.

The projected sales of unsaturated polyester (UPE) resin through 1985 is depicted in Table 4-5. Approximately 80 percent of all UPE produced is reinforced with glass fiber. Approximately 30 pounds of glass reinforced UPE were used in the 1978 American automobile. The 1978 automotive production of glass reinforced UPE was 0.96 billion pounds. This will reach 2 billion pounds⁽⁴²⁾ for autos alone in 1985. This figure may be high since 1985 figures of only 781 million pounds of glass reinforced UPE were projected by Predicasts, Inc. in 1976,⁽⁴³⁾ and only 17 pounds of glass/UPE were identified as being on the 1978 auto by McQuiston in his report to Plastics Engineering.⁽¹³⁾ Probably the most accurate prediction is contained in Gary Goldenberg's article written November 1, 1980, for Plastics Engineering Magazine. Goldenberg estimated 124 million pounds of UPE on the 1979 autos (approximately 99 million

TABLE 4-5
PROJECTED POLYESTER RESIN ANNUAL SALES, 1979-1986 (million pounds)⁽⁴²⁾

<u>Application</u>	<u>1979</u>	<u>1986</u>
Marine	264	328
Transportation	134	380
Construction	266	443
Corrosion	96	165
Electrical	33	55
Consumer	92	150
Furniture and Marble Casting	128	186
Auto Putty	58	88
Other	<u>112</u>	<u>157</u>
TOTAL	1,183	1,952

pounds of glass reinforced UPE). He predicted that the auto industry would utilize 207 million pounds of glass reinforced UPE in 1980.⁽⁴⁴⁾ The figures equate to 31 million pounds of glass fiber in 1979, and 66 million pounds of fiber in 1990. The Goldenberg prediction was made after Detroit decided to exercise the option of "downsizing" in lieu of introducing composites to its autos to decrease weight and hence increase gas mileage.

Phenolic resins reinforced with glass fibers represent another reinforced thermoset. Thirty-seven million pounds of phenolics were used in the 1979 auto. An unidentified but small portion of this material is glass fiber reinforced. The usage of phenolic in autos, both reinforced and unreinforced, is projected to reach 55 million pounds by 1990. They are used for their impact resistance in power tools, brake pads, auto transmissions, and spacecraft. Glass reinforced phenolics are used in vaporizers, pump housings, washing machine agitators, among others.

Glass reinforced epoxies are used for a number of applications such as printed circuit boards and aircraft components. The superior structural properties of epoxies make them especially attractive. The 1990 autos will utilize 30 million pounds of epoxy according to Goldenberg,⁽⁴⁴⁾ a portion of which is glass reinforced.

Other glass reinforced thermosets include silicone resins, alkyd resins, melamines, polyimides, and vinyl esters.

It is obviously difficult to get a firm handle on the future growth of the glass fiber market in the United States. This problem is primarily caused by the rapid changes experienced by the automotive industry in the last three or four years. But it is safe to say that the market is bullish. The major producers of glass fibers are actively pursuing research into the improvement of their product and the development of new markets. Hexcel Corporation is marketing metallized fiberglass fabrics capable of providing lightning strike dissipation for aircraft and Electro magnetic interference shielding for electronics. PPG, Certain Teed, and Owens-Corning are introducing new lines. According to Modern Plastics Magazine, July 1979, U.S. capacity for glass fiber will reach 1.2 billion pounds by 1989.⁽²⁰⁾ Glauz predicts a requirement for 6.195 billion pounds of composite by 2000 or about 2 billion pounds of glass fiber.⁽³⁹⁾

Graphite Fiber Reinforced Plastic Composites--

Applications for graphite fiber reinforced plastics are growing at an extremely rapid pace. This pace has been maintained in spite of the fact that an explosion of automotive applications predicted for the early 1980's never materialized due to the decision by Detroit to increase gasoline mileage through "downsizing."

In the examination of forecasts of the use of advanced fiber composites, the future looks bright. For example, the use of composites in military aircraft may grow from the present five to ten percent of aircraft weight to 30 to 55 percent by the middle 1980's on some aircraft. This growth includes fiberglass and aramids also but graphite will play a major role. In addition, the potential for hybridizing composites with combinations of the three classes of reinforcement looks extremely promising.⁽⁴⁵⁾

At this time the graphite fiber production capacity in the United States is undergoing a significant change. All three major U.S. suppliers of fiber are establishing increased capacity. In the past, there has been a strong reliance on Japan for carbon fiber but the trend has been to bring this capability in-country. In late 1981, Union Carbide plans to begin domestic production of polyacrylonitrile-based (PAN) carbon fibers at a plant being built in Greenville, South Carolina. Union Carbide, the dominant supplier of carbon fiber in the United States, now obtains the PAN-based fibers it sells from Toray Industry of Tokyo. Initial capacity will be 800,000 pounds per year.⁽⁴⁶⁾ Union Carbide bought a petroleum pitch-based graphite fiber plant in 1981. The initial capacity of the plant is 500,000 pounds per year.⁽⁴⁷⁾

The Specialty Materials Division of Avco Corporation has built a carbon fiber production facility in Lowell, Massachusetts. Avco's immediate plans for the facility are to produce less than 100,000 pounds per year.⁽⁴⁶⁾

Hercules, Inc. announced a plan to expand the company's graphite fiber production capabilities to 2.5 million pounds annually at its Bacchus, Utah, plant. The expansion will be completed in 1984. Hercules projects a one million pounds per year capacity in 1982 and a 2.5 million pounds per year capacity in 1984.(48)

Celanese Plastics and Specialties Compaction are building a multi-million dollar PAN-based graphite fiber plant in Rock Hill, South Carolina. The plant will be operational in 1982 and will produce one million pounds of fiber per year.(49) Hitco, a subsidiary of Armco, Inc., produces PAN-based fiber in California at a capacity of about 100,000 pounds per year.(46)

All together the above mentioned manufacturers represent a 1981 U.S. capacity of about two million pounds of fiber per year. Capacity will reach 14 million pounds by 1990, a twentyfold growth over current shipment levels. The generally accepted growth rate of the graphite fiber market among the major producers is 30 to 40 percent per year for the next decade and continued growth through the year 2000 (approximately 10 percent per year). This would result in a projected production of 27.6 million pounds in 1990 and a production of 71.6 million pounds in 2000.

Aircraft Applications of Graphite Composites-- Advanced fiber composite technology has become a fixture in the aerospace industry. Military aircraft are providing leadership in the adaptation of graphite fiber composites. Most of the composites are composed of epoxy matrices with graphite fibers, for example:

- F-15 - 43 pounds of graphite/epoxy
- F-16 - 250 pounds of graphite/epoxy
- F-17 - 900 pounds of graphite/epoxy

The Marines' vertical/short take-off and landing fighter aircraft will have an excess of 30 percent advanced composites in its structure by 1985.(45)

The continuing development of advanced fighter airframe technology is required to develop new structural concepts that are superior in cost/weight performance to more conventional structures. In 1978, NASA began flying to Rockwell-built Highly Maneuverable Aircraft Technology (HiMAT) remotely piloted research vehicles. The HiMAT vehicle is currently designed with about 25 percent of the structural weight of 3,400 pounds, or 850 pounds of graphite/epoxy composite. This vehicle is a test bed for composite applications.(50)

Advanced fighter concepts are being studied by the Air Force. The Air Force Flight Dynamic Laboratory directed four studies that showed the next fighter will contain the range of 40 to 60 percent composites. One version actually reached 80 percent composites. In the wing-fuselage program, the Air Force is aiming for 27 percent weight savings, and 19 percent cost savings.(51) Assuming an average composite range of 4,300 pounds per aircraft and a 60 percent fiber content, an annual production of 200 military aircraft would require 500,000 pounds of graphite fiber per year.(50)

The utilization of graphite fiber by commercial aircraft manufacturers has risen dramatically in recent years. The 1977 graphite fiber usage by the three major U.S. commercial airline manufacturers was 10,000 pounds. This usage reached 60,000 pounds in 1980. By 1988, the projected usage is 180,000 pounds per year. The airliner of the early 1970's weighed 160,000 pounds. With advanced composites this weight could be reduced by 20 percent or become 128,000 pounds. Assuming that 40 percent of the aircraft weight is composites, 60 percent of which is fiber, approximately 31,000 pounds of advanced fiber would be required per aircraft.(51) Finally, assuming that the advanced fiber mix includes 30 percent graphite fiber, each aircraft would utilize 9,000 pounds of graphite fiber. Based on a projected production rate of 360 aircraft per year, the consumption of graphite fiber could reach 3.24 million pounds by the year 2000, or 54 times the present consumption.(52)

Perhaps the two most dramatic applications of graphite fiber composites were for general aviation: (1) Lear Aviation, Inc. has designed and flown an all-composite aircraft, the Lear Fan; (2) the Gossamer Albatross became the first manpowered aircraft to cross the English Channel. The Albatross flight would not have been possible without the use of graphite/epoxy in the main spar for the wing spar. The Lear Fan is also historic. Where the military and commercial aircraft use components of graphite/epoxy in place of metal, the Lear Fan was designed around the use of composites. As a result, it was possible to build an aircraft with a ten-passenger capacity, an empty weight of 3,500 pounds, a range of 2,750 statute miles, and a phenomenal fuel economy of 11 mpg. It is estimated that without composites, the aircraft would weigh 700 pounds more, have a seating capacity of only seven, and an increased fuel consumption of 10 percent. A production level of 300 aircraft per year is projected for the \$1.2 million aircraft by the early 1980's.⁽⁵⁰⁾ Based on 1,000 pounds of graphite/epoxy per aircraft, and a 60 percent fiber weight, this aircraft alone will require 180,000 pounds of graphite fiber per year. Cessna, Grumman, and Piper general aviation aircraft builders are investigating composite applications for their products.

Just as Indy 500 racers have anticipated domestic auto engineering, the Champion soaring planes of the 1960's and 1970's anticipated the high-performance, composite aircraft of the 1980's. One of the first composite sailplanes was designed in 1964 in West Germany. Made of fiberglass and epoxy, it was accorded a mere 200-hour-lifespan by the skeptics, but in tests lasted 50,000 hours! In the early 1970's, the British produced the Kestrel 19 which had graphite fiber wings. The German company, Schempp-Hirth, built a graphite composite sailplane that was flown to second place in the World Sailplane Championships in 1978. Presently, their craft, the Ventus, is sold out through 1982 despite its \$26,000 price.

Space Applications of Graphite Composites-- America's thrust into space in the 1980's will be spearheaded by the Space Shuttle Orbiter. The applications for graphite/epoxy on the shuttle include the Orbital

Maneuvering pods where 300 pounds are saved, and the payload bay doors which represent a 1,070-pound weight savings. This has substantially increased the payload capability of the shuttle.(45)

Utilization of graphite/epoxy composites has increased rapidly in recent years. Over 58 percent of the components on Ford Aerospace's Intelstat V, which was launched in 1979 was composed of advanced composites, primarily graphite/epoxy (approximately 600 pounds). The NASA Space Shuttle payload load retrieval system will be constructed of ultra-high modulus (stiffness) graphite/epoxy. There is great interest on the part of NASA, DARPA, and the Air Force in larger space platforms that will potentially have dimensions in kilometers.(50) For the most part, they will be composed of graphite/epoxy. A single platform of a half-mile square would require 660,000 pounds of graphite/epoxy. This is more than the utilization of this material in 1979.

The Convair Division of General Dynamics Corporation foresees the need for being able to fabricate advanced composite structural materials in pace. According to Convair, a high temperature thermoplastic such as polysulfone, and spools of high strength filament such as graphite would be shipped from earth to orbit. Tubular structural elements would be fabricated in orbit.

Military Applications of Graphite Composites-- Advanced fiber composites are currently being considered for a wide range of military applications other than those already mentioned. This includes Army requirements for mobile bridging which would utilize either graphite/epoxy or graphite/aluminum. Armored vehicles are generally quite heavy. Advanced fiber composites in the superstructure, the tank treads, etc., are being investigated.(50)

The U.S. Navy is looking at graphite/epoxy for their high performance ships such as hydrofoils. Boeing Marine Systems is evaluating graphite/epoxy control flaps for the PCH-1 hydrofoil. It is likely that small patrol craft will be the first test platform for these materials.(50)

Graphite composites are being looked at for a number of electronic applications. These include shipboard antennas. Hercules, Inc. has been awarded a contract to manufacture the launch tube for the MX missile using graphite/epoxy. At a length of 80 feet and a diameter of 8 feet, this is the largest graphite composite structure to date. Each cannister will weigh approximately 23,000 pounds and contain 14,000 pounds of fiber. A fleet of 300 will require 4.2 million pounds of fiber savings in the early 1980's.

Automotive Applications of Graphite Composites-- The manufacturers and developers of graphite/plastic composites envisioned a huge market in the automotive industry prior to 1979. It was at that time that Detroit decided to "downsize" before adding massive doses of composites. Ford Motor Company exhibited at the 1979 SAE Exposition in Detroit an experimental car using graphite/epoxy in place of a number of steel components (Table 4-6). This clearly showed the potential gains achievable with graphite composites. The result of downsizing and high manufacturing costs has postponed the use of graphite composites. If graphite composites are to have a large impact on the auto industry in the first half of the 1980's, it will be in the form of hybrid composites, that is, a combination of graphite fibers and less expensive fibers such as fiberglass.

In summary, the use of graphite composites in automobiles is not expected to be significant before 1990. After 1990, the market size is undetermined. The push towards front-wheel drive eliminates the contending graphite composite drive shaft as a large market. The requirement to reduce 4,000-pound cars to 2,500-pound cars is probably only feasible with graphite composites without reducing volume of the auto and has been scrapped as a strategy. The only hope for graphite would appear to be hybridization with glass fibers to reduce total part cost. Hybrid leaf springs, engine brackets, drive shafts, bumpers, etc., have been tested and look attractive in both price and performance.

The advent of electric vehicles may represent a potential market for graphite composites. The value of a one-pound reduction in weight is at a premium. This is due to the fact that the weight of the power generating

TABLE 4-6
SUMMARY OF COMPONENT WEIGHTS FOR FORD GRAPHITE PROTOTYPE AUTOMOBILE(14)

<u>Component</u>	<u>Weight (pounds)</u>		<u>Savings</u>
	<u>In steel</u>	<u>In graphite</u>	
Body-in-white*	461.0	208.0	253.0
Frame	282.8	207.2	75.6
Front end	96.0	29.3	66.7
Hood	49.0	16.7	32.3
Deck lid	42.8	13.9	28.9
Bumpers	123.1	44.4	78.7
Wheels	92.0	49.3	42.7
Doors	155.6	61.1	94.5
Miscellaneous**	69.3	35.8	33.5

* Complete body structure without closure panels (doors, deck lid, etc.) and trim (seats, etc.).

** Bracketry, seat frame, and other items.

group (motor and fuel or battery) is a much greater fraction of the gross vehicle weight for an electric vehicle (EV) than for an internal combustion engine vehicle (ICE). Additionally, the unit cost of the power generating group is much higher for the EV. Therefore, weight reduction is three times as valuable for an EV as for an ICE. This drives the breakeven price of graphite fibers up to the \$18 to \$20 per pound level. At \$20 per pound Union Carbide's 55 million modulus pitch fiber is on the verge of being economical. DOE is funding a demonstration program which will put 10,000 EV's in service by 1986. An extremely optimistic projection would put the 1990 EV production rate at 25,000 cars per year. This would require 3 to 4 million pounds of high performance fiber,⁽⁵²⁾ or about 1 to 1.33 million pounds of graphite fiber per year.

Miscellaneous Applications for Graphite Composites-- There are a number of additional applications for graphite composites. Some of these have been in existence such as sporting goods, which actually allowed the graphite fiber producers to survive the lean "early days." Other applications, such as musical instruments, are relatively new ventures. Representative applications follow:⁽⁵⁰⁾

- Agricultural machinery
- Material handling equipment
- Industrial machinery
- Abrasive tools
- Chemical plant structures and equipment
- Medical applications
- Scientific equipment

Summary for Graphite Composites-- The discussion above would indicate that the potential market for graphite/plastic composites are as follows:

<u>1985</u>	<u>1990</u>	<u>2000</u>
2.8 million lbs/year	47 million lbs/year	120 million lbs/year

The vast majority of this market is for epoxy matrix composites but other matrix materials will see limited application. Polyester market size is dependent on the auto industry. This market potential has been covered in

the discussion of glass fiber in this section and will not change due to the use of graphite graphite versus glass fibers.

Boron and Silicon Carbide Fiber Reinforced Plastics--

Two additional advanced reinforcements for plastic matrix composites must be evaluated to truly evaluate the future of composites: boron and silicon carbide continuous filaments. Both of these fibers are primarily products of Avco Corporation. In addition, boron is available from Composite Technology, Inc. (CTI). The present capacity for boron filament is 35,000 pounds per year at Avco and 15,000 pounds per year at CTI. The present price of boron filament ranges from \$200 to \$250 per pound.⁽⁵⁴⁾

As stated in Section 3, the primary applications for boron as a reinforcement for plastic are on military aircraft. The matrix plastic is epoxy in every case. Additionally, boron is found in golf clubs, tennis rackets, and fishing poles. Based upon Avco's projection that the carbon core boron filament will drop only slightly by the year 1990 to \$180 to \$225 per pound (in 1981 dollars), it is unlikely that it will be able to compete well with the graphite and Kevlar® reinforcements. The market may grow due to increased defense procurement under the Reagan Administration, 30,000 pounds per year for the F-14, F-15, and development of the B-1, versus only 7,500 pounds per year under Carter.⁽⁵⁵⁾

In contrast, Avco expects its silicon carbide filament to grow dramatically through the year 2000. Present production is only being done on a pilot scale, 200 pounds per year. Avco projects a 1990 market for 50 to 100,000 pounds per year. The price of silicon carbide filament is presently \$390 per pound. But as volumes grow, the inherent low cost of the production process versus the boron process could result in prices as low as \$50 per pound by 1990.⁽⁵⁰⁾ Therefore, this high performance fiber becomes a strong competitor not only with boron but with some grades of graphite. As in the case of boron, the primary reinforcing matrix is expected to be epoxy and, in some minor applications, polyimide.

Kevlar® Fiber Reinforced Plastic Composites--

As covered in Section 2, Kevlar® fiber reinforced composites are classified as "advanced composites." Applications for Kevlar® reinforced composites are growing rapidly. The Du Pont Company, which invented Kevlar®, describes it as the most important fiber since nylon. As mentioned earlier in this report, Kevlar® is light yet so strong that a few strands of it supported the wings of the Gossamer Albatross, the manpowered airplane that flew across the English Channel. Clothing made of Kevlar® is as heat resistant as asbestos. Woven into a vest only three-eighths of an inch thick, Kevlar® can stop a 0.38 caliber bullet fired from a few feet away. Originally developed for the automobile market, Kevlar® has not made much of an impact there due to price. A second market for Kevlar® has been in the area of bullet-proof gear such as vests for police and dignitaries (Henry Kissinger and President Ford both wore Kevlar®-lined jackets). Over 300,000 police officers in the United States have Kevlar® vests. But Kevlar® is still losing money. Du Pont, nonetheless, has made a commitment to expand output to commercial quantities, tripling its capacity to 45 million pounds per year. Du Pont is banking on significant growth in the advanced composites market.⁽⁵⁶⁾ Kevlar® 49 is the grade of filament to be used in the composites. At present, it only represents five to eight percent of the total Kevlar® output of 15 million pounds per year. By 1990, Du Pont is projecting a composite market usage in the millions of pounds, not in the tens of millions.⁽⁵⁷⁾

Aerospace Applications of Kevlar® Composites-- Kevlar's® main hope as a reinforcement component is in energy-related areas (much like graphite). The rising gasoline costs that shattered the market for large automobiles with premium tires, and that has driven up the cost of Kevlar® feedstock could be the salvation of Kevlar®. It is possible to greatly reduce the weight of a structure while in some cases actually making it stronger by introducing Kevlar® reinforced composites. The commercial aircraft field, where a reduction in weight of one pound saves as much as \$300 in fuel over the life of the craft provides an attractive potential market for Kevlar®. Kevlar® is already used on the DC-10, the Lockheed L1011, the deHavilland DHC-7, and the Sikorsky S-76 helicopter. But for the most part the applications are nonstructural such as overhead racks, partitions,

lavatories, galleys, bulkheads, as well as pressure bottles used to activate escape slides and life rafts.⁽⁵⁸⁾ The skyrocketing aviation fuel costs have driven the designers toward the use of Kevlar® in structural applications. The Boeing 767 will use extensive amounts of Kevlar®/graphite/epoxy hybrids.⁽⁵⁹⁾ Du Pont expects Boeing to account for four percent of its Kevlar® production by 1990, 1.8 million pounds per year.⁽⁵⁶⁾ Additional potential commercial aviation applications include jet engine blade containment systems with projected weight savings of 200 pounds per engine, cargo liners and floor panels, cargo containers, and helicopter blades.⁽⁵⁸⁾

In present day and future strategic missile systems, Kevlar® will play a major role. Kevlar®/epoxy filament wound motor cases and pressure bottles are unsurpassed in weight conscious performance. For example, all three stages of the Trident C-4 ICBM are fabricated with Kevlar®. Kevlar® will also be seen in the MX and the Space Shuttle.⁽⁶⁰⁾

Marine Applications of Kevlar® Composites-- Composites reinforced with Kevlar® provide lighter, stiffer, more damage tolerant and vibration damping laminates than glass reinforced plastics for marine applications. Kevlar® usage as reinforced hulls, decks, and bulkheads will continue to grow.

Kevlar® impacts almost all boat markets. The Navy and Coast Guard are investigating the use of Kevlar® for structural and ballistic applications.⁽⁶¹⁾ It has been shown to be cost effective in fishing boats saving in operating costs over the life of the ship.⁽⁶²⁾ Kevlar® reinforcement was used on 90 percent of the bass boats sold by Hydra-Sports, Inc. as early as 1977. Kevlar® reinforced bass boats are faster (one holds the speed record of 80.124 mph) and more efficient than their glass reinforced counterparts.⁽⁶¹⁾ More than 40 canoe and kayak manufacturers now offer models with Kevlar® 49. About 80 percent of the competition canoes and kayaks are fabricated from Kevlar®.⁽⁶¹⁾

The vast majority of the Kevlar® composites used in marine applications use polyester as a matrix. Originally, more expensive vinyl ester had to be used but the advent of polyester compatible finishes for

Kevlar® fabrics eliminated this obstacle.⁽⁶³⁾ Du Pont predicts an ultimate market of 40 million pounds of advanced composites per year in the marine market. This represents as much as 24 million pounds of Kelvar® per year.⁽⁶⁴⁾ This is an optimistic projection in both the size of the marine market (i.e., made before the 1980 depression of marine market) and the ability to displace most of the glass composites.

Automotive Applications of Kevlar® Composites— Kevlar® 49 composites have been evaluated for automotive applications. But due to cost, the potential market is severely limited. Kevlar® presently costs \$10.50 to \$35 per pound depending on denier and is not expected to drop but rather to track inflation.⁽⁵⁷⁾ Hybridization may hold some promise in structural transmission support. Kevlar® hybrids have also been developed for driveshafts, bumpers, leaf springs, radiator supports, wheels, and assorted body parts. Most of these composites would have a polyester matrix.

Kevlar®/phenolic composites show great promise as asbestos-free brakes.⁽⁶⁵⁾ The competition for the asbestos-free brake market is fierce. The trend towards significantly increased usage is well established. The first generation of asbestos-free drum linings for passenger cars and light trucks is in the final stages of development at Bendix Corporation, and is in the initial stages of evaluation by vehicle manufacturers. If these asbestos-free drum linings prove to be commercially acceptable, initial limited production usage could begin as early as 1982. The possible substitutes range from wollastonite at \$1.00 per pound, to graphite at \$98.90 per pound. Kevlar® at \$19.80 per pound is still relatively expensive.⁽⁶⁶⁾ The fact that the tests are complicated, the requirements complex, and the program incomplete make it impossible to predict the market that will become available to Kevlar®, although the overall potential is immense (180 million pounds per year in asbestos brake linings).

Miscellaneous Applications of Kevlar® Composites -- Kevlar® is found in, or has potential for, a number of other applications:

- Sporting goods - hockey sticks, golf shafts, javelins, skis
- Military head gear
- Surfboards
- Flywheels
- Musical equipment

Metal Matrix Composites--

Interest in metal matrix composites has continued to develop as a result of the desire of the Department of Defense (DOD) to obtain high specific strength and modulus materials that can be used in environments where the temperatures exceed the capabilities of polymer matrix composites. The first decade of metal matrix composite development proceeded slowly but positive gains were made. Dr. Ruth Davis, Undersecretary of Defense for Research and Engineering, announced a metal-matrix composite technology thrust at the DOD/Materials Technology Conference on February 21, 1978. This thrust received considerable support from both the U.S. Senate and the House of Representatives. As a result, a five-year tri-service program was initiated. This has resulted in significant strides in metal-matrix composite technology and will result in opening up many new markets for this class of composite materials.

Metal-matrix composites (MMC) have current or potential application in three major areas in the Air Force: aeropropulsion, aircraft and missiles, and space structures. In aeropropulsion, the applications include:

- Boron/aluminum - engine blades and vanes
- Borsic-titanium - blades, vanes, and shafts
- Fiber-reinforced superalloys - engine blades and vanes

Currently, progress in these areas is being impeded by adverse fiber-matrix interactions at elevated temperatures. This is particularly true in reinforced titanium. These reactions may occur during fabrication and/or during use. Several solutions to this problem are being investigated including the use of protective coatings on the fibers such as carbon-rich coatings from silicon carbide monofilament, boron carbide coated boron filament, and silicon carbide-coated boron.

If technical progress continues to be made, F-100 engines may begin by 1990. Fiber requirements for this project are projected to be approximately 23,000 pounds per year.⁽³³⁾

In the area of aircraft and missiles, U.S. Air Force development is directed at selectively reinforced airframe members. Due to the conservative approach normally followed in developing and fielding such components, it is highly unlikely that the U.S. Air Force will field these materials before the year 2000. The present and projected future cost of these materials will also serve to slow progress.

Space structures being developed by the U.S. Air Force generally benefit from the fact that cost is a relatively unimportant factor. Graphite/magnesium and graphite/aluminum materials are being considered by the Air Force for large space antennae and booms. It is estimated that the production of MMC for space applications will be 1,300 pounds per year in 1990 and exceed 4,500 pounds per year in the year 2000.

The U.S. Navy's MMC program is aimed at a number of applications. The first of these is the use of silicon carbide (SiC) reinforced titanium in advanced tactical missiles. Projected materials requirements will be 2,000 pounds in 1995 and 12,500 pounds by the year 2000. For shipboard antennae, the U.S. will use silicon carbide/aluminum and graphite/aluminum. The production time frame is 1982 to 1987, and a production of 42,000 pounds of silicon carbide/aluminum and 16,500 pounds of graphite/aluminum will be utilized.

For hydrospace structures such as advanced torpedos, mines, and submarine batteries, the following MMC materials will be fabricated:

- Graphite/aluminum - 790,000 lbs
- Silicon carbide whisker/aluminum - 1,700,000 lbs
- Silicon carbide/aluminum - 84,000 lbs
- Graphite/lead - 76,500 lbs
- Alumina (FP)/lead - 138,430 lbs

These materials will be fabricated in the 1983 to 1995 time frame.(68)

For strategic missile applications, the Navy will look at guidance platforms, forward adapters, and re-entry vehicle substructures. The MMC materials requirements will be:

- Silicon carbide/aluminum - 120,000 lbs
- Graphite/aluminum - 66,000 lbs

These materials will be produced during the 1990-2000 time period.(68)

Finally, the U.S. Navy projects the production of 1.7 million pounds of silicon carbide/aluminum beginning in 1982 and running through 1987 for ordnance.(68)

The U.S. Army's efforts will focus on helicopter transmission cases and mobile bridging materials. Approximately 120,000 pounds of MMC will be used in helicopters from 1982 to 1993. This will most likely be either graphite/aluminum or FP/alumina. For bridging, approximately 5,000,000 pounds of silicon carbide/aluminum will be needed by 1990.(68)

There are several specialty areas of MMC research that have great promise, but that will not reach fruition until after the year 2000. One example of this type of application would be fiber reinforced superalloys (FRS). This technology would allow turbine blades to operate at temperatures 400°F higher than current superalloy blades. Tungsten-fiber reinforced superalloys show much greater strength than conventional superalloys. Ordinary unalloyed tungsten-lamp-filament wire (type 218 tungsten) makes the composite about 50 percent stronger than the conventional material. There are major problems facing the developers of this composite but advances continue under Navy and NASA sponsorship.(69) Another specialty area lies in hybrid composite blades which combine MMC and polymer composites.

Finally, major advances are being made that could lead to widespread use of metal-matrix composites (MMC). Silicon carbide whiskers are presently being produced by Exxon Enterprises. Work performed at the Naval Surface Weapons Center, Silver Spring, Maryland, indicates that whisker reinforced aluminum composites exhibit properties considerably higher than those of the unreinforced alloy. A number of inexpensive, conventional metals fabrication processes are available to fabricators of silicon

carbide whiskers/aluminum composites. These processes include extrusion, rolling, and forging, among others. Of these, the ones which have been tried appear to yield isotropic hardware with good properties (Table 4-7). The whiskers are produced from rice hulls. The fabrication process has undergone significant improvements and yields of over 90 percent whiskers versus particulate is common.⁽⁷⁰⁾ The overall yield per pound of rice hull has also increased. The present price of the whiskers is now \$95 per pound. The projected price is covered in Table 4-8.⁽¹¹⁾ In 1980, Exxon produced approximately 2,000 pounds of whiskers. Projected future annual production rates are covered in Table 4-9. These projections are based on acceptance of this material which looks promising. The silicon carbide whisker/ aluminum provides a relatively inexpensive intermediate property option to the higher priced continuous filament composites discussed earlier in this section.

Recently, it was discovered that the single inclusion of silicon carbide particulate in aluminum alloys results in rather dramatic increases in mechanical properties. At present this phenomena is under investigation by the Air Force, the Marines, and the Defense Advanced Research Projects Agency. DWA Composites Specialties Inc. is fabricating silicon carbide particulate/aluminum using commercially available silicon carbide powders costing less than \$5 per pound. Parts have been fabricated using diffusion bonding, extruding, and forging. Tensile moduli of 16 to 28 million psi have been achieved, and tensile strengths in excess of 100 ksi are achievable.⁽⁷¹⁾ The present capacity available for this product is 25,000 to 30,000 pounds per year. This will be increased to 50,000 pounds in 1981 if demand continues to grow. In the future, the capacity is almost unlimited due to the fact that conventional equipment can be used. The present price for this material, trade named DWAl"20", is \$100 per pound of composite. This figure is expected to drop to \$50 per pound by the end of 1981 and eventually hit \$10 per pound.⁽⁷²⁾ This material is a dramatic departure from normal MMC, and in fact, it is not really a fiber reinforced composite. Although the properties of DWAl"20" are not fully understood, it is postulated that the platelet shape of the particulate leads to a fiber-type reinforcement. The Defense Advanced Research Projects Agency program should yield valuable data in this area.

TABLE 4-7
MECHANICAL PROPERTY DATA FOR SILICON CARBIDE WHISKER/2024
ALUMINUM-T4(70)

	Percent Volume Fraction Silicon Carbide		
	15	20	25
Ultimate Tensile Strength (ksi)	58-63	66-76	80-93
Tensile Modulus (msi)	13-14	14-17	17-22
Ultimate Compression Strength (ksi)	---	80-100	---

TABLE 4-8
PROJECTED SILICON CARBIDE WHISKER PRICES
(in 1980 Dollars)⁽¹¹⁾

<u>1980</u>	<u>1981</u>	<u>1982</u>	<u>Future</u>
\$95/lb	\$45/lb	\$25/lb	\$5-\$15/lb

TABLE 4-9
SILICON CARBIDE WHISKER ANNUAL PRODUCTION PROJECTIONS⁽¹¹⁾
(in pounds)

<u>1980</u>	<u>1981</u>	<u>1982</u>	<u>1983</u>	<u>1984</u>	<u>1985</u>
2,000	7,000	20,000	100,000	500,000	500,000- 1,500,000

As indicated in this section, the primary reinforcing fibers for MMC will be: silicon carbide (continuous, whisker, and particulate), boron, graphite, and alumina (FP). The continuous fibers of silicon carbide and boron result in the ultimate MMC properties. The total U.S. capacity for boron filament is approximately 50,000 pounds per year (35,000 pounds at Avco and 15,000 pounds at Composites Technology, Inc.). The present price of boron filament ranges from \$200 to \$250 per pound. In 1981 dollars, the price is projected to drop to \$180 to \$225 per pound and it is expected to drop further by the year 2000. The principal reason for the drop in price is economies of scale, which will be realized by the increasing size of the market. This will be especially true if the Reagan defense budget is approved and the annual requirement for boron goes from 7,500 pounds per year under Carter to 30,000 pounds per year.⁽⁵⁴⁾ The continuous filament carbon core silicon carbide filament, produced by Avco and by a German firm and marketed by Fiber Materials, Inc. in the United States, could displace boron in a number of applications. The present U.S. continuous filament capacity is only about 200 pounds per year. If market demand follows projections, capacity will reach 50,000 to 100,000 pounds of filament per year. It should continue to grow through the year 2000. The high hopes for silicon carbide filament are based on its combination of high strength and modulus and projections of low price. The present price is \$390 per pound, but this is expected to fall to \$50 per pound by 1990 and even lower by 2000.

Carbon Matrix Composites--

As mentioned in Section 3, carbon matrix composites are a specialized class of composites. Basically, they have been used where polycrystalline graphite cannot be used. Most carbon composites (carbon/carbon) are used in advanced aerospace applications such as re-entry vehicle ablatable nosetips, leading edges of the space shuttle, rocket nozzles, and exit cones. The major commercial application to date has been as aircraft

brakes for fighter aircraft and the Concorde. Current production of carbon/carbon brake materials is about 10,000 pounds per month. This will increase as the new commercial airliners, such as the Boeing 757 and 767, go into service. Carbon/carbon composites will be used as divergent flaps on F-100 jet engines to replace columbium parts presently in service. It is possible that in five years these flaps could be produced at a rate of 1,000 per month representing an annual production of 132,000 pounds.(33)

Additional possibilities for carbon/carbon composites are: nuclear reactor components, fusion reactor components, bone and heart implants, components for use in petroleum refining equipment, small gas turbine engine vanes and blades, and perhaps major sections of the aft end of jet engines. The key to a number of these applications would be the ability to coat or treat the composite to significantly reduce its rate of oxidation.

The overall use of carbon/carbon composites will remain relatively restrained due to the fact that the material is expensive to produce, highly energy intensive, and production rates are extremely low (e.g., it takes 4.5 months to fabricate a military brake, shoe, and up to six months to produce a three-dimensionally reinforced carbon/carbon rocket nozzle).

Ceramic Matrix Composites--

Ceramic matrix composites are being investigated for a number of applications:

- Reinforced ceramic turbine blades for ground-based gas turbines
- Laser-resistant dielectric materials
- Advanced antenna windows
- Laser mirror substrates

For the most part these materials are specialized in nature and will only see use in military applications. Reinforcements include alumina fiber, quartz fiber, graphite fiber, and boron nitride fiber. Matrices include quartz, boron nitride, alumina, silicon carbide, and silicon nitride. Potential quantities are extremely small for the major military

applications and they would not be produced in quantity until well beyond the year 2000 on the ground-based turbines (also applicable to advanced cruise missiles).

SUMMARY

In summary, the future for fiber reinforced composites is very hopeful. Advanced reinforcement, such as graphite, is expected to expand at extremely high rates through the year 2000. This is confirmed by the unusually large amount of capital growth in the graphite fiber industry, with all three major manufacturers expanding to meet demand. An annual growth rate of 30 to 40 percent to the year 1990 and 10 percent to the year 2000 is anticipated by the industry. Similar growth projections for Du Pont's Kevlar® fiber (Du Pont is investing \$250 million over the next two years on plant expansion) portend significant growth. This growth is graphically depicted in Figure 4-5. Figure 4-6 depicts the projected growth of the three major matrix materials, epoxy and unsaturated polyester and vinyl ester. The projected growth rate for epoxy is predicted by the industry to be 6 to 8 percent per year for the foreseeable future. Depending on the optimism of the predictor, the growth rate of unsaturated polyester could be any of several numbers covering a relatively wide range, the more optimistic figure being 12 percent. It is felt that the rate will be 2 to 4 percent per year, unless new markets not presently in existence are developed. A similar growth rate was predicted for vinyl esters. Based on data obtained in the course of this effort an eight percent growth rate was assigned to epoxy resins.

When compared to the market share held by fiberglass, the reinforcements investigated remain insignificant through the year 2000 (i.e., the fiberglass market share is 99.6 percent and only drops to 96 percent in the year 2000). But, the fiberglass market share may become the market of the more advanced fibers since the crucial first step of replacing a homogeneous material such as a metal with a reinforced material would already have been taken.

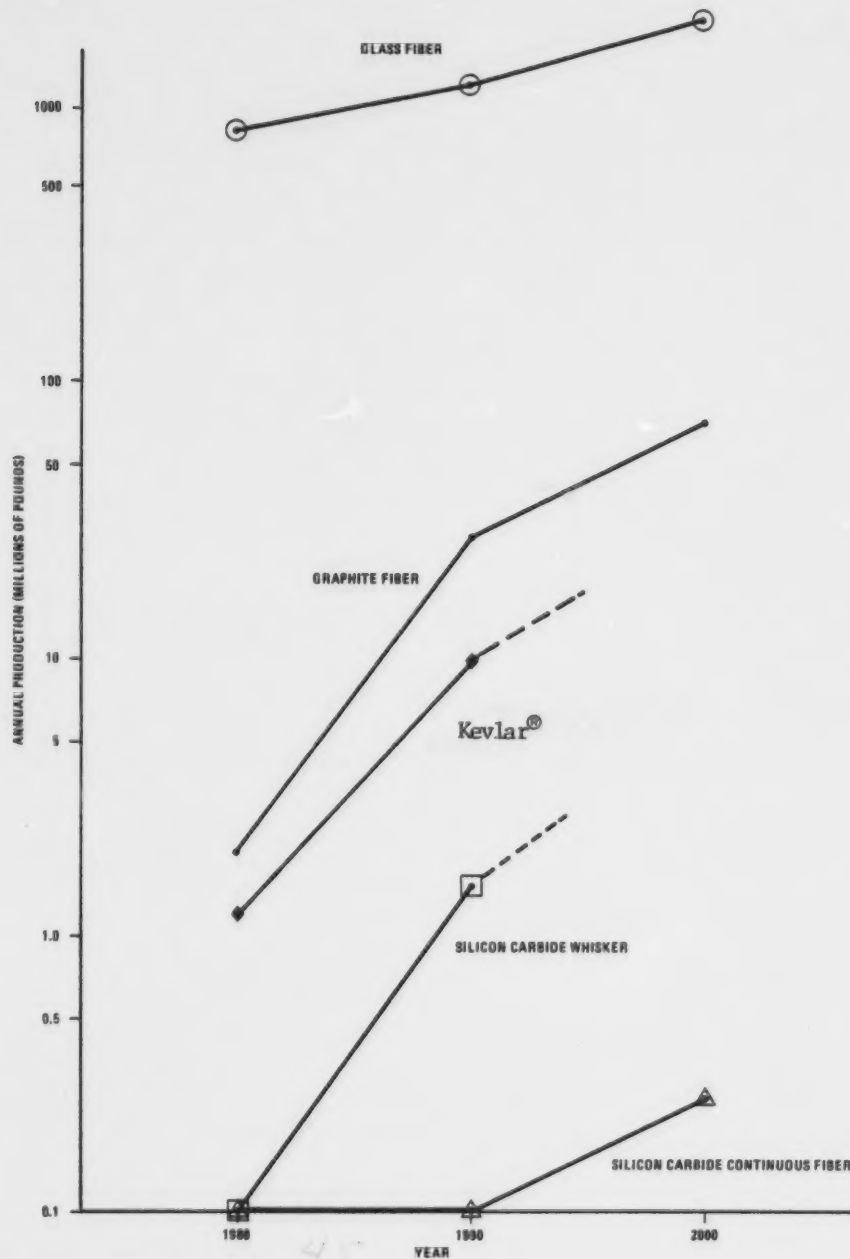


FIGURE 4-5. REINFORCING FIBER ANNUAL PRODUCTION 1980-2000 (SEMI-LOGARITHMIC)

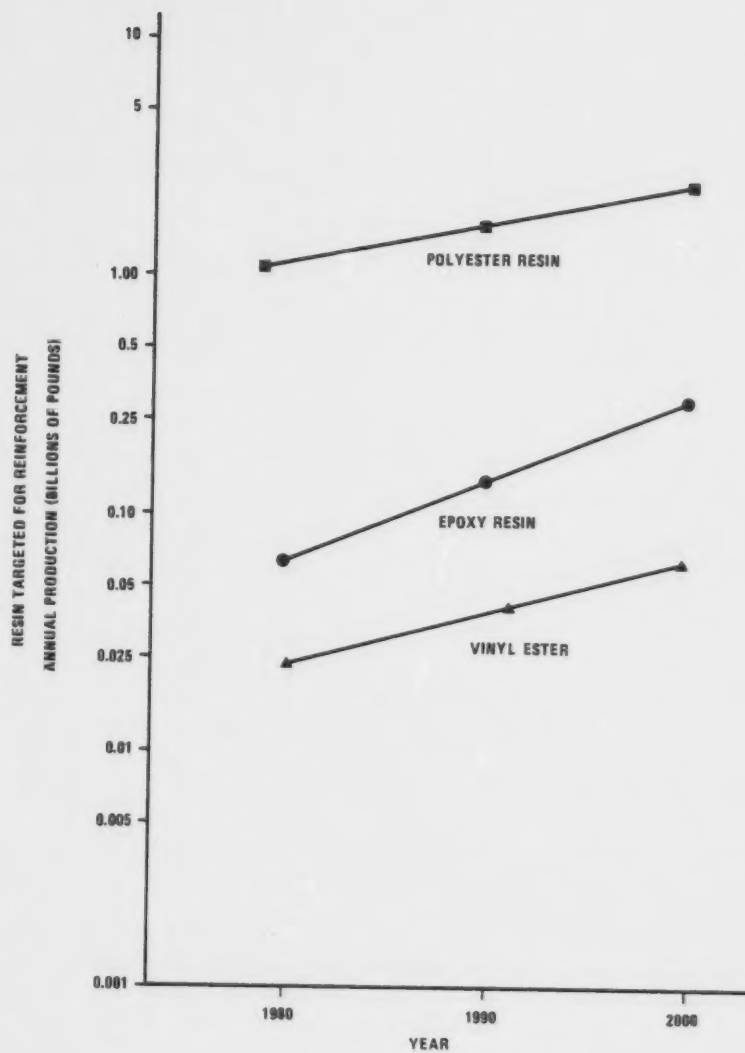


FIGURE 4-6. MATRIX RESIN ANNUAL PRODUCTION 1980 - 2000 (SEMI-LOGARITHMIC)

SECTION 5
HAZARD ASSESSMENT

METHODOLOGY

The hazard assessment methodology, utilized in the course of this program was designed to assess the impact of composite materials over the time period from 1981 to the year 2000. Initially, a background and literature search was performed to:

- (a) Provide a basis for identifying and analyzing future trends in the use of composite materials.
- (b) Provide a data base for assessing the potential public health and environmental risks associated with composite materials usage trends.

The data base assembled included data on the following:

- Types of composites (current and future use).
- Production (present and future).
- Users (present and future).
- Supply and demand trends.
- Results of controlled toxicological studies.
- Clinical observations of accidental exposures.
- Epidemiological data.
- Physical, chemical, and biological impacts on air, water, and land.
- Global, regional, and local effects, including the effect of composite materials on indoor air quality.
- Relevant environmental transport data.
- Pertinent EPA regulations.

It was found that, due to a paucity of toxicity data, it would not be possible to perform a quantitative risk analysis. Therefore, only a qualitative assessment could be made.

Starting with the 30 materials listed below, an analysis was initiated to screen out materials which would see little or no use by the year 2000.

● Matrices

Plastic

Epoxy

*Polyimides

*Phenolics

*Epoxy/Novolacs

*Melamines

Vinyl esters

Polyester

*Polysulfones

*Polyphenyl sulfones

*Polyamide/imides

*Polycarbonate

*Polyphenylene sulfide

*ABS

*Nylon

*Polyether sulfones

Metals

*Aluminum

*Magnesium

*Titanium

*Superalloys

Ceramics

*Carbon

*Silicon Nitride

*Boron Nitride

*Silica

*Glass

● Reinforcing Fibers

Graphite

Aramid (Kevlar®)

Glass

*Boron

*Boron nitride

Silicon carbide (fiber and whiskers)

Eight materials (epoxy resin, polyester resin, vinyl ester resin, graphite fiber, Kevlar® fiber, glass fiber, silicon carbide fiber, and silicon carbide whiskers) were selected for further analyses. Epoxy and polyester resin systems already enjoy widespread use in composite systems and this use is projected to grow dramatically, hence they were retained. Graphite and Kevlar® are the two most promising reinforcements for "advanced fiber composites," therefore warranted further investigation. Glass fiber presently composes 99 percent of all fibrous reinforcements.

* Denotes materials eliminated in initial screening.

This relative proportion is expected to change relatively little through the year 2000. Finally, vinyl ester and silicon carbide fiber and whiskers have great potential to make a significant impact on the overall composites market.

Each material was evaluated in light of 3 scenarios: (1) use, (2) recycling, and (3) combustion. For these eight materials quantifiable data on toxic effects and exposure were not available. Data on production processes, consumptive uses, environmental disposal and qualitative toxicity data were available and incorporated into the monographs (Appendixes A through G).

Based upon the qualitative data available, the eight materials were assigned to one of the following four groups with the recommended follow-up actions for each group:

Group 1 includes materials or their combustion products which have not been listed as hazardous by EPA or for which no health or non-health* hazard has been identified to date; therefore, further investigation can be postponed in favor of materials in higher priority groups.

Group 2 includes materials or their combustion products which have been identified as presenting some potential for nonhealth related hazards and, therefore, further investigation may be warranted to resolve the uncertainties.

Group 3 includes materials or their combustion products which have been identified as presenting some potential for health-related hazards and, therefore, further investigation

* The only non-health hazard of concern is the shorting-out of transformers and other electrical equipment caused by the discharge of carbon fibers into the atmosphere as a result of the incineration of graphite fibre reinforced composites.

is warranted to resolve the uncertainties. Follow-up actions might involve making scientifically comprehensive risk assessment and consideration for inclusion in the appropriate EPA list and/or investigation to identify safe combustion practices.

- Group 4 includes materials or their combustion products that have been included on an existing EPA toxic or hazardous substances list.

Interpretation of Results for Fibers

Graphite Fibers--

The U.S. market for graphite fiber reinforced composites in 1981 is expected to be approximately two million pounds. This will rise to about 72 million pounds by the year 2000. The principal application for these composites are aerospace, automotive, and sporting goods in that order. The fibers are in all cases imbedded in a matrix that is principally epoxy in the case of plastic composites, aluminum in metal matrix composites, graphite in carbon/carbon composites, and glass in ceramic matrix composites. In all cases, the fiber and the matrices are relatively inert in normal use. The inertness of the fibers is a function of their chemical make-up, which in most cases exceeds 98 percent carbon by assay. The fact that graphite fiber composites are under intense investigation worldwide as implants and prostheses, for such applications as artificial joints, lends added support of their inertness. The only avenues for release of the fiber to the atmosphere would appear to be accidental or intentional burning away of the matrix, which is only a problem with a plastic matrix, or release through frictional wear in the case of applications such as brake shoes.

In 1972, in Fostoria, Ohio, the accidental incineration of raw carbon fiber led to the fallout of conductive fiber. Electrical shorts and damage to circuit elements in the surrounding distribution system was experienced as far away as six miles. This incident, as well as other information concerning the electrical characteristics of graphitized carbon fiber, gave

rise to a coordinated National Action Plan involving a number of federal agencies.⁽⁸⁹⁾ Based on the risk assessment data generated, airborne carbon fibers present a small, definable risk to electrical equipment. The expected effect nationally due to carbon fiber release from aircraft accidents was estimated to be about \$5,600 per year for 1993, with the average loss per incident on the order of a few cents.⁽⁷³⁾ Any health hazard associated with the fiber released during such an incident is undefined. It was postulated that since graphite fibers have relatively large diameters (6-8 microns), their health effects are limited to skin, eyes, and upper respiratory tract irritation. However, it has been noted that horizontal cleavage of fibers can occur during mechanical manufacturing applications and potentially can lead to smaller fibers becoming airborne which could penetrate more deeply into the lungs, thus constituting a greater respiratory hazard.⁽⁷⁴⁾ Whether or not this cleavage and release is possible in brakes is a possibility, but no data on its probability were located. Without mechanical damage, as in normal use, there would appear to be no way for the fibers to be released.

To date, two independent toxicology studies have been conducted using carbon fiber.^(88,89) One study reported on the long-term toxicity of carbon fiber implants in rats and mice. The test period was 18 months for mice and 24 months for rats. Histological examination was carried out on all tissue sections for implant areas and for specific organs removed at post-mortem examination. Only one malignant tumor (fibro-sarcoma) was found in relation to an implant. In the other study, guinea pigs were exposed to airborne chopped carbon fibers for time periods up to a maximum of 104 hours. About 99 percent of the airborne particles generated were nonfibrous and about one micron in diameter. Few of the airborne fibers observed were of a respirable size (reported as 1.0-2.5 microns diameter and less than 100 microns long). Animals were sacrificed at intervals ranging from 1 to 144 days. No tumors were observed.

The current method for disposal of carbon fiber or carbon fiber reinforced composites is by landfill. Over the next decade, an increasing

amount of carbon fiber composite material will be introduced into municipal waste streams. A portion of this waste will be incinerated. The effectiveness of exhaust gas particle removal systems in limiting the emission of carbon fiber is not yet determined.

Finally, it is not considered feasible to recycle graphite composites. Fiber damage is unacceptable and would eliminate the advantage of going to graphite fibers in the first place.

In summary, based on two toxicology studies (88, 89), graphite fiber use is not expected to pose exposure or toxicity problems except in the workplace. Therefore, the use of graphite fibers is assigned to Group 1, materials for which hazard appears low. The combustion of graphite fiber and graphite fiber containing composites is assigned to Group 2, materials for which there is some potential of non-health related hazards.

Kevlar® Fibers--

Kevlar® fibers are only produced by E. I. Du Pont de Nemours & Co., Inc. Current capacity is 7,500 tons and is expected to reach 22,500 tons by 1982. The major applications are in aerospace, aircraft, boats, and marine applications.

No data are available on the environmental fate or degradation products of Kevlar® fibers.

No evidence of skin sensitization was found when Kevlar® was tested on guinea pig skin under occluded conditions or in a 200-subject prophetic patch test on human skin. No skin irritation was found after 48 hours of continuous contact. Some irritation, probably from mechanical causes, did occur after 144 hours of continuous occluded contact.

Some processing operations might generate fly, small airborne particles. These operations could include, for example, machining. However, the material which may be seen is expected to fall out and not remain airborne, and is outside the range considered respirable. DuPont has concluded that:

1. Concentration of elongated particles and total dust were low compared to existing standards for nuisance and allergenic dust, and were in the range of standards for fibrogenic dust; and

2. Based on animal inhalation tests, respirable dust from Kevlar® produced what would be considered a typical lung reaction to a nuisance dust particulate.⁽⁷⁵⁾

No further toxicological data on Kevlar® itself are available. It should be pointed out that the manufacture of reinforced plastics involves the handling of dozens of resins, solvents, curing agents, accelerators, thixotropic agents, etc., each with its own potential hazard.⁽⁷⁶⁾ Laboratory vapor inhalation tests have indicated that one of the in-process solvents, hexamethylphosphoramide (HMPA) used in Kevlar® manufacture, will produce cancer in rats.⁽⁷⁷⁾ There is no evidence that this solvent or its vapor has caused cancer in humans. In any case, any residual HMPA that may be retained by Kevlar® after processing is reportedly too tightly bound to the fiber to present a serious inhalation problem.⁽⁷⁶⁾

The combustion products of Kevlar® were determined in 1976 in a series of fast and slow pyrolysis experiments.⁽⁷⁸⁾ Fast pyrolysis in a 650°C furnace produced approximately 63 percent carbon monoxide, 35 percent benzene, and 2 percent toluene. Slow pyrolysis produced at least 15 compounds and a series of nitrogen-containing cyclic compounds. These included nitrogen, carbon monoxide, carbon dioxide, methane, ethylene, propene, benzene, toluene, benzonitrile, aniline, methylaniline, phenylacetonitrile, phthalonitrile, phenyldiamine, biphenyl, benzimidazole, fluorene, and benzanilide. No ammonia or hydrogen cyanide were observed. No trace of residual HMPA was observed at sensitivities down to 1 ppm.

Tatem and Williams⁽⁷⁹⁾ studied the combustion product profiles of Kevlar® and a Kevlar®-resin system under three types of thermal stress: direct flame impingement under atmospheric oxygen, and thermal radiation under both atmospheric (21 percent) and low (10 percent) oxygen conditions. The two sample types were a Kevlar® blanket and a Kevlar® plus Derakane® 510 resin system. The main gaseous products identified were aliphatic and aromatic hydrocarbons.

The three stresses were chosen to encompass several conditions that might exist in a typical fire. Kevlar® began to degrade at 475°C. The oxygen concentration at and beyond this point has an effect on the nature of the combustion products evolved. It may be possible for Kevlar® to be exposed to heat from a fire but not directly to flames in an environment with reduced oxygen concentration; in the case of a fire under reduced or nonexistent ventilation, atmospheric oxygen can be rapidly consumed resulting in oxygen-deficient combustion. Tables 5-1 and 5-2 show the products of combustion under the different conditions of the experiment.

The products acrolein, styrene, and ethylbenzene were produced only by the Kevlar®-resin system. The high yields of styrene and ethylbenzene are not surprising, since Derakane® 510 is a vinyl ester containing 40 percent styrene. The "worst case" for the system in terms of the quantity of these chemicals released is represented by thermal degradation at 21 percent oxygen. Acrolein is highly toxic (lethal in a short time at concentrations as low as 10 ppm) but is a lachrymator and will serve as its own warning agent. Trace amounts of propionitrile were liberated by the system under 10 percent oxygen; the highly toxic effects of this compound are intensified by its ability to be absorbed through the skin.

Small amounts of hydrogen cyanide and hydrogen chloride were released from Kevlar® alone under direct flame impingement.

Although some risk problems may arise during the production process of the fibers, Kevlar® fibers do not appear to pose a risk during normal use of materials containing these fibers. Therefore, with respect to usage, Kevlar® fibers are assigned to Group 1, materials for which hazards appear low.

In summary, the combustion of Kevlar® fiber reinforced composites resulted in the release of several toxic materials such as benzene, toluene, hydrogen cyanide, and hydrogen chloride. The relative toxicity of these compounds has not been determined. In the case of combustion, therefore, Kevlar® is assigned to Group 3, materials for which there is some potential for a health related hazard due to the formation of identified toxic substances under certain combustion conditions, and therefore further investigation is warranted to identify safe combustion practices.

TABLE 5-1
CHEMICAL COMPOUNDS GENERATED FROM EXPOSURE OF KEVLAR® +
DERAKANE® 510 RESIN SYSTEM TO VARIOUS STRESSES

Compound	Peak No.**	Structure	Mg of Product/Gram of Sample Consumed*		
			10% Oxygen Thermal	21% Oxygen Thermal	Hydrogen Torch
Methane	1	CH ₄	0.36	1.3	0.67
Unknown	2	—	—	—	—
Ethene	3	CH ₂ =CH ₂	0.27	1.1	0.58
Acetylene	4	HC≡CH	0.01	0.02	3.0
Ethane	5	CH ₃ -CH ₃	0.04	0.19	—
Propene	6	CH ₂ =CH-CH ₃	0.8	3.2	0.02
Propane	7	CH ₃ -CH ₂ -CH ₃	+	+	+
Unknown	8	—	+	+	+
Unknown	9	—	+	+	+
Unknown++	10	—	0.65	2.4	—
1-Butene	11	CH ₂ =CH=CH ₂ CH ₃	0.62	1.8	—
Butane	12	CH ₃ (CH ₂) ₂ CH ₃	—	—	—
Unknown	13	—	—	—	—
Acetonitrile	14	CH ₃ CN	+	+	0.01
Acrolein	15	CH ₂ =CHCHO	1.7	4.5	+
1-Pentene	16	CH ₂ =CH(CH ₂) ₂ CH ₃	0.53	1.8	—
Acetone	17	CH ₃ COCH ₃	1.5	5.9	0.06
Pentane	18	CH ₃ (CH ₂) ₃ CH ₃	+	+	+
Unknown	19	—	+	—	—
Unknown	20	—	+	—	—
Propionitrile	21	CH ₃ -CH ₂ CN	+	—	—
2-Hexene	22	CH ₂ =CH(CH ₂) ₃ CH ₃	+	+	—
Hexane	23	CH ₃ (CH ₂) ₄ CH ₃	+	+	—
Unknown	24	—	+	—	—
Unknown	25	—	+	+	—
Benzene	26	C ₆ H ₆	0.07	0.95	1.2
Unknown	27	—	+	+	—
Unknown	28	—	+	+	—
Toluene	29	C ₆ H ₅ CH ₃	0.91	6.2	0.07
Ethyl benzene	30	C ₆ H ₅ CH ₂ CH ₃	1.5	6.6	0.46
Styrene	31	C ₆ H ₅ CH=CH ₂	52	108	44
Unknown	32	—	+	+	+
Unknown	33	—	+	+	+

* HCL and HCN analyses are accurate to within 20%; all other analyses to within 5%.

** Peak numbers refer to chromatograms in Figures 2 and 3.

— Absent

+

++ Calculated as 1-butane equivalents

Source: Tatem and Williams, 1979

TABLE 5-2
CHEMICAL COMPOUNDS GENERATED FROM EXPOSURE OF KEVLAR®
BLANKET TO VARIOUS STRESSES

Compound	Peak No.	Structure	Mg of Product/Gram of Sample Consumed*		
			10% Oxygen Thermal	21% Oxygen Thermal	Hydrogen Torch
Methane	1	CH ₄	0.06	0.19	0.58
Unknown	2	—	—	—	+
Ethene	3	CH ₂ =CH ₂	0.09	0.21	0.38
Acetylene	4	HCECH	—	+	0.32
Ethane	5	CH ₃ -CH ₃	+	0.01	0.03
Propene	6	CH ₂ =CH-CH ₃	0.02	0.07	0.10
Propane	7	CH ₃ -CH ₂ -CH ₃	+	+	0.10
Unknown	8	—	+	+	+
Unknown	9	—	—	+	+
Unknown++	10	—	0.38	0.82	0.07
1-Butene	11	CH ₂ =CH-CH ₂ CH ₃	0.34	0.60	0.07
n-Butane	12	CH ₃ (CH ₂) ₂ CH ₃	+	+	0.04
Unknown	13	—	+	+	+
Acetonitrile	14	CH ₃ CN	—	0.04	0.48
Acrolein	15	CH ₂ =CHCHO	—	—	—
1-Pentene	16	CH ₂ =CH(CH ₂) ₂ CH ₃	0.13	0.42	0.01
Acetone	17	CH ₃ COCH ₃	+	0.45	0.08
Pentane	18	CH ₃ (CH ₂) ₃ CH ₃	+	0.02	0.07
Unknown	19	—	—	—	—
Unknown	20	—	—	—	—
Propionitrile	21	CH ₃ -CH ₂ CN	—	—	—
2-Hexene	22	CH ₂ =CH(CH ₂) ₃ CH ₃	0.01	0.02	0.01
Hexane	23	CH ₃ (CH ₂) ₄ CH ₃	0.01	0.02	0.01
Unknown	24	—	—	—	—
Unknown	25	—	—	—	—
Benzene	26	C ₆ H ₆	—	0.03	4.4
Unknown	27	—	—	+	+
Unknown	28	—	—	+	+
Toluene	29	C ₆ H ₅ -CH ₃	—	0.19	0.42
Ethyl benzene	30	C ₆ H ₅ -CH ₂ CH ₃	—	—	—
Styrene	31	C ₆ H ₅ CH=CH ₂	—	—	—
Unknown	32	—	—	+	+
Unknown	33	—	—	+	+
Unknown	34	—	—	+	+
Hydrogen Chloride		HCl	—	—	0.08
Hydrogen Cyanide		HCN	—	—	0.10
Carbon Dioxide		CO ₂	22	21	980
Carbon Monoxide		CO	2.1	10	25

* HCL and HCN analyses are accurate to within 20%; all other analyses to within 5%.

— Absent

+

++ Calculated as 1-butene equivalents

Source: Tatem and Williams, 1979

Finally in the area of recyclability, the mechanical properties of recycled Kevlar® fiber would be greatly reduced. One recycling process would be the mechanical crushing of a composite and the resolidification of the crushed particulate into a new part through the introduction of additional matrix material. The current disposal technique is landfilling.

Silicon Carbon Fibers--

The U.S. market for silicon carbide fibers in 1980 was extremely small, only 200 pounds of continuous filament and 2,000 pounds of whiskers. These figures are projected to rise to more than 100,000 pounds of filament and 1,000,000 pounds of whiskers per year by the year 1990. The principal applications are aerospace and military.

In all cases the fibers will be embedded in a stable matrix, either a metal (aluminum, magnesium, super alloy, etc.) or epoxy. With the exception of machining, it is unlikely that fibers would be released to the atmosphere under normal use. Silicon carbide is relatively inert. Most reactions only occur at high temperature (Table 5-3). Toxicity data on these fibers are not available. The size of the fibers, especially the whiskers which are as small as one micron in diameter in the case of Exxon's whiskers formed from rice hulls and under one micron for some of the deposition type whiskers, could result in respiratory effects. Mearl F. Stanton of the National Cancer Institute indicated that since neoplastic response to a variety of types of durable fibers, particularly asbestos fibers, was similar, NCI's experiments reinforce the idea that the carcinogenicity of fibers depends on dimension and durability rather than physicochemical properties and emphasized that all respirable fibers be viewed with caution.⁽⁸⁰⁾ In 1977, Stanton indicated that the probability of pleural sarcoma from silicon carbide implantation was 100 percent.⁽⁸¹⁾ He indicated that fibers that are fine and long may be more carcinogenic than others simply because they are uncompromised by phagocytic activity (the activities of a cell which has the ability to ingest and destroy particular substances).⁽⁸²⁾ Although these data are not conclusive and there are laboratory data that contradict these data, the possibility of

TABLE 5-3
REACTION OF SILICON CARBIDE

<u>Reagent</u>	<u>Temperature</u>	<u>Reaction</u>
Hydrochloric acid	Boiling	None
Hydrofluoric acid	Boiling	None
Sulfuric acid	Boiling	None
Fuming nitric acid	Hot	None
Oxyhydroben blast	Fused	Slow oxidation
Air	1,000°C	Slow oxidation
Lead chromate	Fused	Slow oxidation
Calcium oxide	1,000°C	Is attached
Magnesium oxide	1,000°C	Is attached
Sodium silicate	1,300°C	Is attached
Potassium carbonate	Fused	Decomposes
Alkali sulfates	Fused	Decomposes
Borax	Fused	Decomposes
Cyrolite	Fused	Decomposes
Potassium hydroxide	900°C	Forms silicon tetra- chloride and carbon
Copper oxide	800°C	Forms metal silicide

carcinoma exists. Based upon the fact that the fibers are generally not free to travel due to the fact that the matrix is metallic and not easily removed, the likelihood of health hazards related to use of silicon carbide whiskers composites would appear to be extremely small.

The combustion of silicon carbide reinforced composites is not feasible for metal matrix composites but could be used as a disposal technique for epoxy composites. The fibers would not be destroyed in the combustion process and therefore would become part of the residue which would then have to be landfilled. The airborne particulate problem posed by whiskers would not arise since it is not envisioned that epoxy composites would not be reinforced with whiskers but only with silicon carbide continuous filament.

The prospect for recycling of silicon carbide filament does not appear to be economically attractive because of the difficulty of extracting useable fiber from the matrix.

Silicon carbide fibers, with respect to use and combustion, are assigned to Group 1, materials for which the potential for hazard is extremely low. It should be noted that care should be taken in the handling of loose whiskers and the machining of whisker reinforced composites due to possible carcinogenicity of inhaled particulate.

Fiberglass--

The U.S. market for fiberglass reinforcement was approximately 0.8 billion pounds in 1980. This figure will exceed 1.9 billion pounds by the year 2000. The largest application for glass composites will be in land transportation principally private automobiles.

In all cases, the fibers will be embedded in a plastic matrix, primarily polyester and epoxy. With the exception of machining, it is unlikely that they would be released to the atmosphere under normal use conditions. Machining is probably the only likely activity that could result in the release of fibers.

The pathological effects of glass fibers have been studied in great depth. The fiber size determines whether or not it can be inhaled and

subsequently cleared out of the body. Most studies to date have addressed the relatively large fibers used in the insulation industry. Most of the fibers are too large to be inhaled deeply, although insulation workers' lungs are contaminated with small fibers also. In addition, it is difficult to extrapolate from this industry to the remainder of the glass fiber industry or to the general population, since many health problems arising from the inhalation of glass fibers are related to the concomitant inhalation of organic solvents used as glues. Although fibrous glass morphologically resembles the asbestiform silicates, its biological action potential is considerably less. The one exception to this rule is fine glass fiber. Extremely slender glass fibers are injurious to lung tissue especially if the fibers are relatively long. The combination of glass fiber inhalation exposure with tubular infection or silica exposure, have a potential synergistic effect. Fibrous glass, however, does not have the capacity to cause lung cancer or act as a carcinocinogen even with beryllium salts which are themselves highly carcinogenic.⁽⁸¹⁾ G. W. H. Schepers reported that the responses of four species of experimental animals to the prolonged inhalation of two varieties of fiberglass-reinforced polyester plastics indicated that, although not wholly devoid of capacity to provoke tissue changes, fiberglass/polyester behaved generally like comparatively inert substances.⁽⁵⁴⁾ In addition, it should be noted that no identified cases of occupational bronchitis have been linked to exposure to glass fibers. Based on this information in the area of use, glass falls in Group 1, materials for which the potential for hazard is extremely low.

Recycling of glass fiber composites has come under recent scrutiny by the automotive industry. Currently, almost all nonmetallic portions of scrapped vehicles are disposed of as landfill. The need for natural resource conservation combined with the escalating costs of landfill has resulted in a search for most cost-effective approaches. These include: (1) incineration for disposal, (2) recovery of energy as steam or electricity by burning, (3) recovery of chemicals and of fuels by pyrolysis and hydrolysis, and (4) reuse. The reuse option is extremely limited in

utility. This is due more to the matrix material than to the glass fiber and will be covered in the section that follows on polyester. Recycling of these materials would appear to be limited to energy recovery through burning. The actual energy would result from the combustion of the plastic matrix material. The glass would melt under normal incineration processes and potentially form a slag that would have to be landfilled. It would be possible to go to a two-stage incineration process where the fibers would not be melted but the plastic would be volatilized for burning in a second stage of the incinerator. In summary, the hazard potential of the fiber in incineration could only come about through the release of fibers. But, this problem is amenable to pollution control (i.e., wet scrubbers, cyclones, baghouses, or combinations). Therefore, the combustion of glass fiber reinforced composites from the standpoint of the fiber was placed in Group 1, materials with no identifiable potential for hazard.

Interpretation of Results of Resins

Epoxy Resins--

The worldwide capacity for epoxy resins is estimated to be 440,000 tons with over 70 percent of this capacity belonging to three American firms. In 1979, U.S. production of epoxy resins for composites amounted to 53 million pounds. The major applications for epoxy resins reinforced with graphite, glass, or Kevlar® fibers are in the aerospace and automotive industries.

Data are not readily available to assess the toxicity of epoxy composites. There is some concern that workers such as those working in automotive repair shops may be exposed to dust from the machining of epoxy resins. A result of inhalation of these dusts may be pulmonary tissue reactions and lung disease.⁽⁹⁰⁾ Dermatitis may also be a problem to workers during the manufacture of the epoxy resins, but dermatitis has not been determined to be a problem to users of epoxy resins.

No data are available to determine toxic effects of epoxy resins and epoxy advanced composites to the consumer under normal exposure conditions.

The epoxy resins have been approved by the Food and Drug Administration as liners for food storage. Therefore, the epoxy resins are expected to be inert and not pose a leaching problem into foods.⁽⁸³⁾

The technology to recycle plastics waste for reuse is not yet economical. The cost of recovery, purification, and reformation into a new product of consistent quality does not seem feasible at this time. It is, however, under study by the chemical, automotive, and aerospace industries. Actual data on the feasibility of recycling for reuse epoxy composite materials are not available.

The most feasible technique for recycling of epoxy would be to recover energy for steam and electricity by burning. Epoxy resins have also been evaluated to determine their toxicity due to thermal decomposition. The tests were conducted for an uncontrolled burning situation. The animals tested died of the carbon monoxide formed as a combustion product. Table 5.4 presents the pyrolysis products of epoxy resin.⁽⁹¹⁾ Based upon this information, it is possible to generate toxic compounds through the combustion of epoxy. If the epoxy is burned in an approved incinerator, it should pose no problem.⁽⁸⁴⁾ However due to the possibility of uncontrolled burning, epoxy resin is assigned to Group 3, materials with a finite possibility of a health related hazard due to the formation of identified toxic substances under certain combustion conditions. Further investigation is warranted to identify safe combustion practices.

Polyester Resins--

The 1979 consumption of all reinforced polyesters was reported to be 1.75 million pounds. The polyester advanced composites are mainly used in the automotive industry, with smaller amounts being used by the aerospace industry.

Few data are available on the environmental degradation of polyesters. Glass-reinforced composites perform well during chemical resistance tests indicating a high degree of stability. Polyester resins involve styrene monomers, consequently, the physical hazards of handling

TABLE 5.4
ANALYSIS OF VOLATILE PRODUCTS FROM
PYROLYSIS OF EPOXY RESIN⁹¹

<u>Component*</u>	<u>Amount in Volatile Products**, Percent by Weight</u>			
	<u>At 360 C</u>	<u>At 500 C</u>	<u>At 800 C</u>	<u>At 1200 C</u>
Hydrogen	—	—	0.8	2.1
Carbon monoxide	4.7	3.1	11.2	25.9
Carbon dioxide	16.2	6.0	3.7	1.8
Methane	1.0	0.8	1.6	4.3
Acetylene	—	—	—	2.5
Ethylene	—	—	3.0	3.0
Acetone	0.9	2.2	—	—
Propane	—	1.1	—	—
Propylene	6.5	2.3	2.2	—
Ethane	—	—	1.6	—
Cyclopentadienes	—	—	—	0.6
Pentanes	—	0.5	—	—
Benzene	—	1.3	2.8	8.1
Methyl chloride	5.1	—	—	—
Ethyl chloride	1.7	—	—	—
Others (not shown)	—	0.7	0	0.8
V _{pyr}	63.6	82.0	73.1	50.9
	—	—	—	—
TOTAL	100.0	100.0	100.0	100.0
Volatilized part of sample, percent	38	75	86	87

*Components in amounts of less than 0.5 percent are not shown

**Percentages are based on weight of total volatilized part.

polyester resins are mostly those associated with the styrene component. Overexposure to the vapors from this liquid can lead to irritation of the respiratory tract and possibly to anesthesia. Due to the disagreeable odor at relatively low vapor concentrations and the accompanying nasal irritation at low concentrations below those needed to cause systemic effects, willful inhalation of toxic amounts of styrene is quite unlikely.⁽⁸⁵⁾ Toxicological studies on animals have shown that seven-hour exposure to relatively high concentrations of styrene vapors (200 ppm or less) does not cause organic injury. The threshold for odor detection of styrene monomer is considered to be in the range of 1 to 10 ppm.⁽⁸⁶⁾

Overall reaction of laboratory animals to fiberglass/polyester particulate inhalation indicated that although there is some capacity to provoke tissue changes, in tests the substance behaved like comparatively inert substances. This would seem to indicate that even the machining, probably the only environment where fibers and resins are airborne, is relatively innocuous.⁽⁵⁴⁾ Additionally, since there would be no styrene vapor emanating from polyester composites, toxic effects would be expected to be negligible in the area of use. Therefore, polyester is assigned to Group 1 regarding its use as a matrix for composites.

Combustion and recycling of polyester composites are related subjects in that both address the handling of scrap materials, the vast majority of which will come from junk automobiles. Currently, most all nonmetallic portions of scrapped vehicles are disposed of as landfill. However, the escalating costs of landfill as well as the projected volumetric growth of this component has resulted in a search for more cost-effective approaches. These include: (1) incineration for disposal, (2) recovery of energy as steam or electricity by burning, (3) recovery of chemicals and/or fuels by pyrolysis and hydrolysis, and (4) reuse. Approximately eight million cars will be scrapped annually affording roughly 220 million pounds of plastics; principally polyester, polyurethanes, polypropylene, other thermosets, ABS and others.⁽⁸⁷⁾ About 125 auto shredders in the United States process approximately three million vehicles into three fractions:

1. Ferrous fraction (iron and steel) - recovered by shredders.
2. Non-ferrous fraction - shipped to Huron Valley steel Corporation for separation into zinc, aluminum, copper, and nonmetallics;

e.g., plastic, rubber, wood, and paper. Nonmetallic materials are used as landfill.

3. Air fraction - low density plastics and rubber used as landfill.

Landfill is the principal current method of disposal. The need for resource conservation clearly demands more viable solutions in the future. Consequently, other methods have received considerable attention:

- Incineration and Burning

Incineration traditionally has been looked upon as a disposal rather than recycling technology, although energy recovery by burning of mixed municipal refuse is receiving much attention lately: Plastics possess a higher energy content (10,000-20,000 Btu/lb) than mixed municipal refuse (5,000 Btu/lb), and compares favorably with that of crude oil and coal. In fact, at least several cities in Illinois, New York, and Tennessee burn refuse to generate electricity. Three to four pounds of average municipal waste can produce enough steam to generate one kwh of electricity. Based on information available, it appears uneconomical to deal with burnable car scrap except as combined with municipal refuse.

In any case, while the resin content of plastics can be recycled as heat and energy, the filler portion (minerals, glass) will invariably result in a landfill residue.

- Material Recovery

Pyrolysis or destructive distillation in the absence of oxygen is a process in which a material is heated to drive off volatile (useful) components and leave a char consisting mainly of carbon and ash. Some pilot development projects suggest that pyrolysis of mixed municipal refuse may be commercially feasible, although the systems cannot accept plastics as part of the municipal waste stream without further process development. Laboratory studies with waste plastics (Union Carbide and others) show that pyrolysis produces low molecular weight polymers, greases, petrochemicals,

coke, and burnable materials from all the major plastics now produced. In the case of polystyrene and acrylics, it may be feasible to recover the monomer for the manufacture of new resin. Pyrolysis is not yet a sufficiently technologically advanced process for economic material recovery from automotive plastics mixtures although it will assume greater importance both as the volume of automotive plastic scrap increases and as the need for resource recovery becomes more urgent. In a 1972 study, pyrolysis appeared closer to technological feasibility than any municipal waste sorting system.

In a recent joint Ford Motor Corporation/University of Tennessee development program, plastic scrap was pyrolyzed to obtain 42 percent by weight of liquid hydrocarbons, 42 percent char residue and 8 percent gas with a heating value of 300 to 400 Btu/cu. ft.

- Reuse

In the past, the Bureau of Mines has explored salt water flotation techniques to further separate plastic scrap. Due to aging, most of the separated materials (PVC, ABS, polypropylene, etc.) exhibit reduced physical and mechanical properties. The cost of material recovery, purification and drying, and reformulation into a product of consistent quality precludes its reuse as an automotive material.⁽⁸⁷⁾

The most promising recycle technology would appear to be burning for energy. Several studies of the relative toxicity of polyesters pyrolysis products have been conducted.⁽⁹¹⁾ One study used glass-fiber reinforced polyester with an antimony oxide flame-retardant added. The toxicity of the combustion products to rats was dependent on the temperature used, and deaths were attributed to carbon monoxide poisoning. At 600°C the pyrolysis products of this composite were lethal to eight of the twenty rats, whose blood carbon monoxide levels were 56 percent. The polyester in this test was, however, less toxic than an equal amount of spruce wood.

Some toxicity experiments with the combustion and decomposition products of self-extinguishing polyester resins have been recorded.⁽²²⁾ Six white mice were exposed to the fumes from the burning of Type 200 FR Alsynite, which is a chopped glass fiber reinforced polyester. Those exposed for 30 minutes to the burning polyester showed nasal irritation, lachrymation, and in some instances became unconscious, but all recovered when exposed to air.⁽⁹¹⁾ No attempts were made to determine the constituents of the combustion or decomposition products. Table 5.5 presents the combustion and decomposition products of polyester. Based upon the data obtained, the combustion of polyester containing composites is assigned to Group 3, materials with a potential for producing toxic combustion products. Further investigation designed to identify safe combustion practices is therefore warranted.

Vinyl Ester Resins--

Vinyl esters are a specialized group of unsaturated polyester resins. U.S. production of the unsaturated polyester resins was estimated to be 20 million pounds in 1980. The major applications include chemical process and storage tank fans, blowers, hoods, fume scrubbers, duct systems, and exhaust stacks.

Due to the superior mechanical, heat resistance, and chemical resistance properties of vinyl ester resins, breakdown is not anticipated to occur even under the most extreme environmental conditions. According to Shell Chemical Company vinyl ester based systems, even after exposure to corrosive environments for up to two years, often exhibit greater strength properties than the initial values of other resin systems.⁽⁸⁵⁾

Vinyl ester resins are solutions of epoxy-based methacrylate esters in styrene monomer. As with polyester resins, the physical hazards of handling vinyl ester resins are mostly those associated with the styrene component.⁽⁸⁵⁾

TABLE 5-5
COMBUSTION AND THERMAL DECOMPOSITION PRODUCTS OF
FIRE-RETARDANT POLYESTERS¹

Material Burned, 22.7 Grams	Sampling Period	Concentration, Percent by Volume					Chlorine and Phosgene
		Oxygen	Nitrogen	Carbon Dioxide	Carbon Monoxide	Hydrogen Chloride	
Fire-retardant polyester "Hetron 93LS"	First	18.2-18.7	79.3	2.0-2.5	0.0031	0.0093-0.0101	Nil
	Second	18.9-19.3	79.2-79.4	1.5-1.7	Nil	0.0012-0.0015	Nil
Fire-retardant polyester "Hetron 92"	First	19.1	78.8	2.1	0.0019	1.0024	Nil
	Second	19.5	78.8	1.7	Nil	Nil	Nil
Phthalic polyester	First	18.9-19.0	78.7-79.0	2.0-2.4	0.0021-0.0024	—	Nil
	Second	19.5-20.2	78.8-79.0	1.0-1.5	Nil	—	Nil

Skin contact with vinyl ester resins for periods of several minutes should cause no irritation.(86) Depending upon the severity of exposure, prolonged contact may cause some irritation and possibly some swelling of the skin. Blistering has been reported to occur when clothing or shoes wet with these materials was worn. Contact of vinyl ester resins with the eyes may irritate the conjunctival membranes and may cause minor corneal injury. The acute oral toxicity of vinyl ester resins has been reported to be low and the chance of ingestion is remote.

No information on toxic effects from use of vinyl ester advanced composites was found in the course of this study. Since there would be no styrene vapors emanating from vinyl ester advanced composites, toxic effects would be expected to be negligible. Therefore, vinyl ester has been assigned to Group 1, materials with low potential for hazard with respect to use.

The recommended disposal method for the specific vinyl ester resins identified to be used in advanced composites is controlled burning in an approved incinerator or burial in an approved landfill. In the landfill situation, leaching is not expected since tests conducted by Shell Chemical show that even after the vinyl ester resins are exposed to corrosive environments, they often exhibit greater strength properties than the initial values of other resin systems.(86)

The argument presented for burning polyester for energy also applies to vinyl ester and hence is the recommended long-term recycling approach. In the area of combustion little or no toxicity data are available. Based upon the data associated with polyester, vinyl ester is placed in Group 3 for combustion.

Table 5-6 shows a summary of the ranking for the action alert materials.

TABLE 5-6
SUMMARY OF GROUP RANKING FOR ACTION ALERT MATERIALS

M A T E R I A L	G R O U P	
	USE	COMBUSTION
Graphite Fiber	1	2
Glass Fiber	1	1
Silicon Carbide Fiber	1	1
Kevlar® Fiber	1	3
Epoxy Resin	1	3
Polyester Resin	1	3
Vinyl Ester Resin	1	3

Group 1 = Materials or their combustion products which have not been listed as hazardous by EPA or for which no health or nonhealth hazard has been identified to date.

Group 2 = Materials or their combustion products which have been identified as presenting some potential for nonhealth related hazards.

Group 3 = Materials or their combustion products which have been identified as presenting some potential for health related hazards.

Group 4 = Materials or their combustion products that have been included on an existing EPA toxic or hazardous substances list.

SECTION 6

RECOMMENDATIONS

Based on the results of the hazard analyses performed on the eight materials that were singled out as the major components of composite materials and reinforced plastics, no actual health or environmental hazard was identified. This applied across the board to all eight materials with respect to use. In the area of combustion, three of the materials appear to pose no hazard. The combustion products of four components, Kevlar®, polyester resin, epoxy resin, and vinyl ester resin have some potential of being hazardous. The production of toxic by-products, such as benzene, toluene, hydrogen cyanide, and hydrogen chloride, indicates that a potential exists. However, it was not possible to quantify this threat or to judge the level of hazard because of a paucity of combustion product toxicity data. Furthermore, it is highly likely that safe combustion practices can be identified for each of these materials.

Graphite fibers were found to present a possible non-health related hazard with respect to combustion. If large numbers of graphite fibers are released to the atmosphere during the combustion process these may result in damage to nearby electrical equipment due to thin electrical conductivity. They were, therefore, assigned to Group 2.

An analysis of the recycling options open to composite materials indicated that the most economically and environmentally attractive recycling option would be burning for energy. The technology needed to first of all strip plastics from scrapped automobiles is being developed by the Bureau of Mines. The economic ramifications of this option are being

closely scrutinized by the major auto manufacturers. It should be noted that the major component of plastic retrieved from autos is not a composite but primarily homogeneous plastics. The introduction of fibers to the burning refuse adds to the complexity of the process. Combusted graphite fibers may present electrical hazards. Combusted glass fibers can generate a slag. Kevlar® generates combustion products with a potential for health hazard.

It is, therefore, recommended that the EPA concentrate any follow-up activities on combustion processes that are environmentally safe and economical when fibers are added to the feedstock. The first priority is to evaluate the toxicity of the combustion products of Kevlar®, polyester, epoxy, and vinyl ester. The second priority is to develop safe combustion processes for those found to yield toxic combustion products. The final priority is to identify combustion processes whereby the release of graphite fiber to the atmosphere is obviated.

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APPENDIX A
GRAPHITE FIBERS

GRAPHITE FIBERS

1.0 INTRODUCTION

Graphite fibers are carbon fibers that have been subjected to heat treatment at temperatures of 2,200 to 2,700°C. The resultant crystalline structure is basic to the properties that make graphite a useful component in advanced composites (NASA 1978). The time-temperature history of the fiber determines its degree of graphitization and properties, though the terms "carbon fiber" and "graphite fiber" are often used interchangeably. Varying the treatment process results in many possible combinations of strength and modulus; this property of variability is unique to graphite among the composite-component fibers.

Graphite fibers are composited with a number of matrices, which may be metals or resins, depending upon the requisite properties. Current applications involve mostly graphite-epoxy composites, within which the characteristics of the graphite are varied. High strength-to-weight and stiffness-to-weight ratios are the primary advantages of graphite fiber composites in general. The fibers are available as continuous or chopped strands or may be woven or prepregged (resin-impregnated).

TABLE 1-1
CHEMICAL DATA SHEET

Name - graphite fibers, carbon fibers

Trade Names* - Fortafil

Thornel

GY70

Magnamite

Panex

Celion

MODMOR

Grafil**

Hyfil**

Torayca**

Kureha**

Beslon**

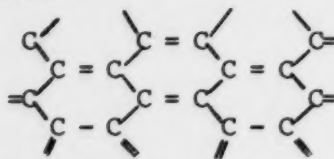
Carbolon**

Wonderfil**

Rigalor**

Sigrafil**

Structural Formula***



Empirical formula - C

* Trade names used by foreign producers.

** Source: NASA, 1978.

*** Source: Kirk-Othmer, 1953.

2.0 ECONOMIC FACTORS

PRODUCTION

Manufacturing Process

Graphite is formed by passing precursor fibers through a series of controlled ovens. The fibers are arranged in tows of 1,000 to 160,000 fibers; the graphite fibers are approximately 4-12 m in diameter. The time and temperature regime determines the properties of the fiber produced: the higher the temperature, the greater the degree of graphitization and the higher the modulus. As the modulus increases, however, the fiber strength generally decreases. Figure 2-1 is a simplified outline of the graphitization process. Precursor preparation processes vary widely between the precursor fiber types.

Three types of precursors are currently in use: rayon, polyacrylonitrile (PAN), and pitch. Rayon-based graphite is largely a product of the past. PAN-based fibers currently comprise the majority of the graphite produced. Pitch is considered to be the future of the industry. Developing technology is expected to make pitch-based graphite economically attractive.

World Production

Worldwide production capacity in 1976 was reported to be 900 tons, with projected 1977 capacity at 1,500 tons. The graphite fiber industry was operating at 40 percent of capacity in 1976, or 360 tons; sales were reported to total 300 tons that year. A projected 400 percent increase in demand and production by 1980 would place world production at 3,600 tons (Kaiser, 1978). Table 2-1 lists the nations producing graphite fibers and their 1976 capacity and sales figures.

U.S. Production and Major Producers

U.S. sales in 1976 were approximately 126 tons, slightly less than half the capacity of U.S. manufacturers. Table 2-2 lists the major producers of graphite fibers in the United States, their approximate sales

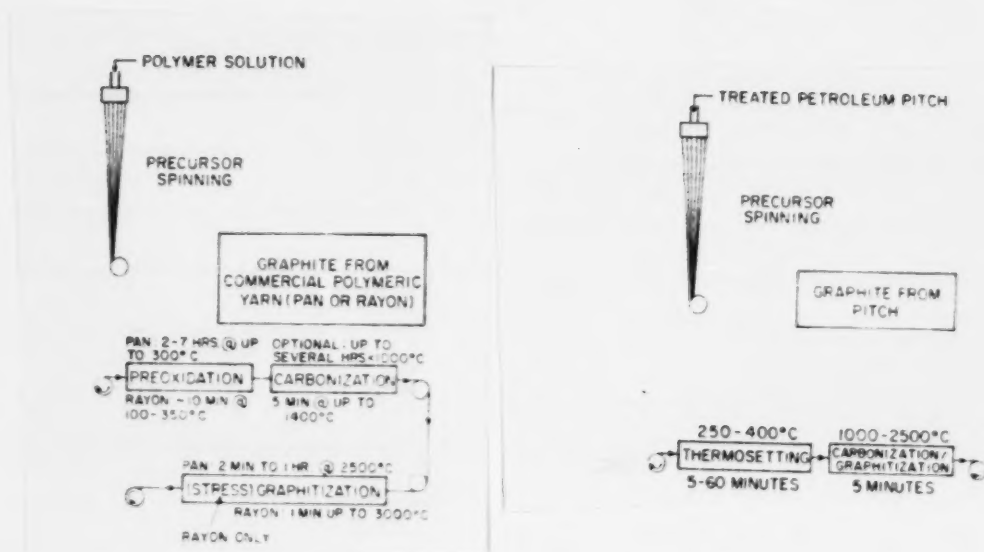


FIGURE 2-1. Carbonization/graphitization processes (Ross, 1976).

TABLE 2-1.
WORLD PRODUCTION AND SALES* (Thousands of Pounds)

<u>Country</u>	<u>1976 Capacity</u>	<u>1976 Sales</u>
United States	627	280
United Kingdom	249	47
Japan	827	364
France	49	NA
Federal Republic of Germany	9-22	9

* Production data for other producers (e.g., USSR) not available
 NA - Not available
 Source: NASA, 1978

TABLE 2-2.
U.S. SALES OF GRAPHITE FIBERS, 1976 (lbs)

<u>Manufacturer</u>	<u>Share of Market, %</u>	<u>Sales*</u>	<u>Type of Product</u>
Union Carbide	45-50	135,000-150,000	high strength, high modulus
Hercules	20-25	60,000-75,000	high strength high modulus
Celanese	10-15	30,000-45,000	high strength ultra high modulus
Stackpole	10-15	30,000-45,000	high strength high modulus
Great Lakes Carbon	5-10	15,000-30,000	high strength high modulus
Others	Balance	5,000-30,000	---
Total		300,000	

* Sales = Market Share (%) x Total Sales (300,000)
Source: NASA, 1978

for 1976, and their product types. In 1976, production was approximately 40 percent of capacity (NASA, 1978). It is estimated that the 1980 market for graphite fibers in the United States, 1,000,000 pounds, is equal to current production capacity. A 30 percent growth rate in graphite fiber demand is projected over the next ten years (Lynch, 1980). Figure 2-2 illustrates the projections in graphite fiber production.

Prices and Trends

The price of graphite fibers depends upon the demand. It is expected that graphite fiber composites will find more applications in the 1980s and, as volume increases, will drop in price. The differences in price between fiber types are a function of energy costs; very high modulus fibers are treated at higher temperatures, resulting in more fuel use and higher cost (Kaiser, 1978). Table 2-3 presents current and projected prices for graphite fiber types. After 1980, PAN prices will probably no longer drop but will increase at a rate less than inflation.

TABLE 2-3.
CURRENT AND PROJECTED GRAPHITE FIBER PRICES*

<u>Fiber Price</u>	<u>Type</u>	<u>1980 Price</u>	<u>1990 Price</u>
PAN 3000 filament**	High strength	\$30/lb	\$30/lb
PAN 15,000 filament**	High strength	\$18/lb	\$12/lb
PAN (unspec.)***	Ultra high modulus	\$110-150/lb	NA
Pitch**, ***	Fiber form	\$20/lb	\$8/lb
	Mat form	\$7-8/lb	NA

NA - not available

* 1980 Dollars used in \$/lb prices

** Lynch, 1980

*** Kaiser, 1978

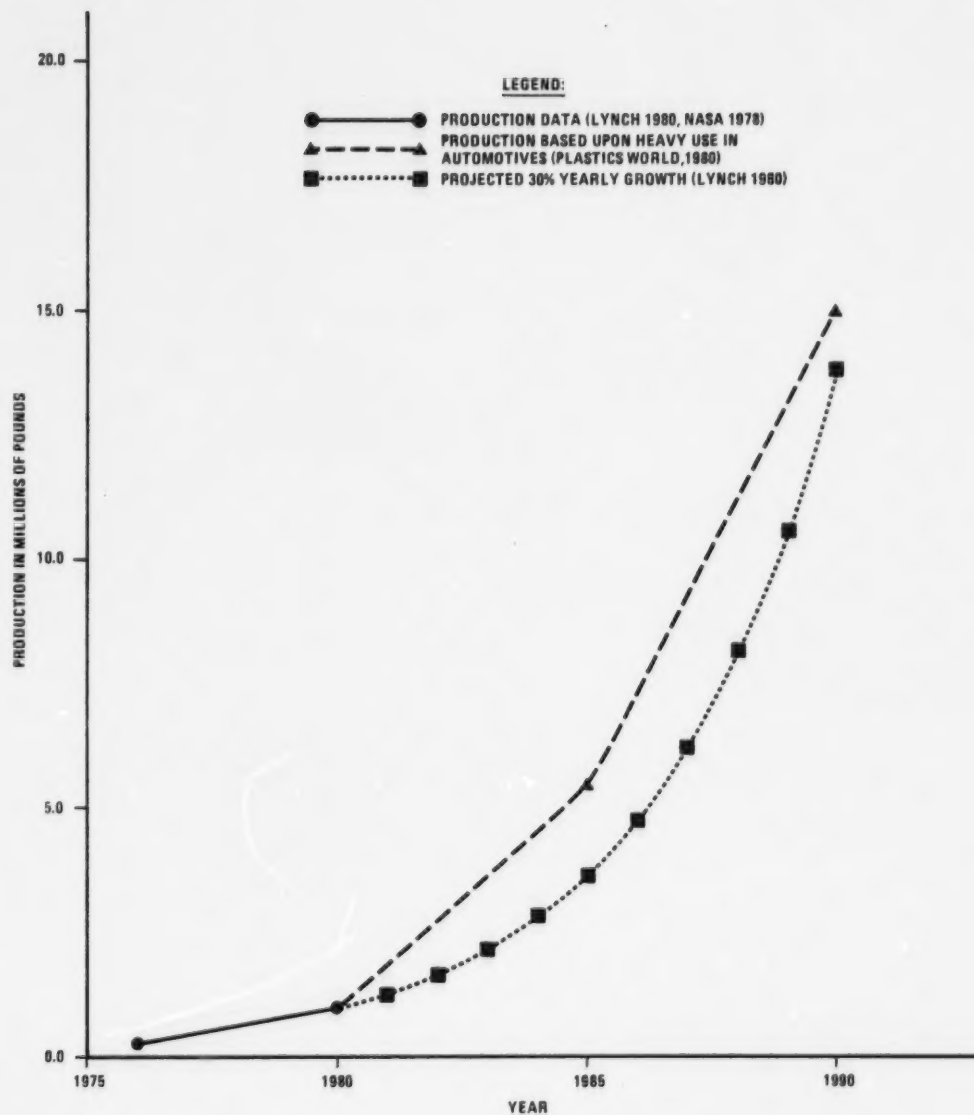


FIGURE 2-2. PROJECTED TRENDS IN U.S. GRAPHITE FIBER PRODUCTION

CONSUMPTION

Major Uses

A given material is selected for use because the required function is performed at acceptable cost and with an acceptable degree of risk. Graphite fiber composites are chosen when the requirements for low weight, high tensile strength, high stiffness, or high fatigue strength outweighs the increased cost incurred by its use (Watts, 1980).

Use of graphite composite materials in military and commercial aircraft is currently their major application. Graphite-epoxy composites are used in three structural groups in aircraft: wing components, empennage components, and fuselage components. Element-by-element substitutions of composites for metals comprise the majority of these applications. Table 2-4 lists current aircraft applications of graphite composites.

Graphite composites are currently in use in NASA's Space Shuttle and in other spacecraft and satellites. The Shuttle utilizes approximately 5,000 pounds of graphite composite components; its cargo doors are the largest single component ever fabricated from graphite composite materials. Both commercial and military satellite systems utilize graphite composites. Communications satellites are especially well-suited to graphite composite applications (Kaiser, 1978).

Sports and recreational equipment manufacturers have successfully employed graphite composites in a number of products. Golf shafts, archery bows, hockey sticks, racing paddles, fishing rods, racquets, ski poles, and some competition snow skis are fabricated from graphite composites (Sittig, 1980). These uses for many years provided the base market advanced composite manufacturers needed to operate their facilities (Watts, 1980).

Minor Uses

Table 2-5 lists some of the minor uses of graphite fiber composites. The applications are largely experimental and specialized and comprise a small portion of the market.

TABLE 2-4.
CURRENT AIRCRAFT APPLICATIONS FOR ADVANCED COMPOSITE MATERIALS

<u>Component</u>	<u>Source</u>	<u>Composite</u>	<u>Weight Savings</u>
Wing			
F-15	McDonnell Douglas	Graphite epoxy	25%
C-5A leading edge slat	Lockheed-Georgia	Graphite epoxy	22%
F-5 landing gear door	Northrop	NA	36%
737 spoilers	Boeing	Graphite epoxy	15%
A-4 landing flap	McDonnell Douglas	Graphite epoxy	47%
F-5 leading edge flap	Northrop	NA	32%
B-1 leading edge slat	Lockheed-Georgia	Graphite epoxy	35%
Empennage			
A-4 horizontal stabilizer	McDonnell Douglas	Graphite epoxy; glass-graphite hybrid	28%
F-5 horizontal stabilizer	Northrop	Graphite epoxy	23%
F-4 rudder	McDonnell Douglas	Graphite polyimide	NA
DC10 upper aft rudder	McDonnell Douglas	Graphite epoxy	37%
L1011 vertical fin	Lockheed	Graphite Kevlar® hybrid	25%
Fuselage			
A-7 speed brake	Vought Aeronautics	Graphite epoxy	40%
F-5 speed brake	Northrop	NA	23%

NA - not available
Source: Watts, 1980

TABLE 2-5.
MINOR USES OF GRAPHITE FIBER COMPOSITES

X-ray support systems and film holders
Scientific instruments (micrometers)
Musical instruments (Ovation guitar)
High fidelity systems (pickup arm, speaker cones)
Automotive (spoilers, hood scoops)

Source: Watts, 1980

Electromotive brushes
Conductive papers and plastics
Electrodes
Blood filters
Synthetic joints and prostheses

Source: Sittig, 1980

Projected Uses

Future uses of graphite composite materials will include expansions of current uses as well as new applications. Some projected uses include automotive, textile machinery (weaving), framework and mechanical parts in drilling rigs, and corrosion-resistant machinery for chemical manufacturing (Kaiser, 1978).

Use in automobiles and trucks is expected, but it is not now known to what extent composites will be incorporated into future designs. The light weight of graphite fiber composites makes possible greater fuel efficiency, but Detroit automakers have opted for downsizing cars to reduce weight (Lynch, 1980). Downsizing also permits automakers to continue using metal-fabricating equipment. The large-scale use of composites would require major capital investments in new machinery and technology development (Goldenberg, 1980). The outlook for graphite fibers in this industry is thus poor until the 1990's. Spokesmen for one major manufacturer indicate that a price of \$4 to \$6 per pound would create more interest in graphite fibers. Another automaker considers the less expensive glass fiber materials to be adequate, although there is some possibility that glass-graphite hybrids may be used in the future (Davies, 1980). One use of graphite composites that had been projected is in drive shafts for rear-wheel drive automobiles (Goldenberg, 1980). The growth of front-wheel drive has negated this demand somewhat, although use of composite drive shafts in trucks is currently under investigation (Davies, 1980).

Other automotive uses of graphite being studied include passenger car frames (Sidwell, et al., 1979), prop shafts, leaf springs, engine brackets, and bumpers (Cross, 1979), and truck frame rails (May and Tanner, 1979). A prototype 1979 Ford LTD has been constructed with graphite composite body, chassis, and powertrain components. The prototype weighed 2,504 pounds, some 1,246 pounds less than the standard model and achieved a 33 percent improvement in fuel economy [Harwood, et al. (no year)] (Bonnett, et al., 1979). The graphite components tested thus far have performed well; only price and the lack of production technology impede the use of advanced composites.

Possible Alternatives

Possible alternatives to graphite fiber as a reinforcing material include glass, boron, and aramid fibers. Hybrids of two fiber types may be used in place of graphite only when specifications allow.

3.0 ENVIRONMENTAL

Graphite fibers are inert, nonbiodegradable, and resistant to incineration. The composites are stable and release few fibers to the environment through normal use (Hoggett, 1974). The major pathway of introduction of these fibers to the environment is incineration of graphite-resin composites; the resins generally burn off completely, and fibers settle, are trapped in smokestack screens, or are released to the atmosphere (Bell, 1980; Sussholz, 1980). Graphite composite products disposed of in landfills would probably release few fibers, though no data are available to substantiate this hypothesis.

The incineration of graphite composite materials results in the formation or release of volatile organic compounds as well as micron size carbon fibers. Table 3-1 presents the data from a study of the pyrolysis products of carbon fibers. There is great variation between the products of different fiber types, probably depending upon the degree of graphitization (Bazinet, et al., 1976; Wagman, et al., 1979). The graphite fibers used in advanced composites are highly graphitized and probably produce only carbon dioxide upon pyrolysis.

The major hazard involved with release of graphite fibers to the atmosphere is the possibility of damage to electrical or electronic components by the conductive fibers. A program conducted by NASA has studied the rate of release of carbon fibers from burning graphite composites and evaluated the risk to electrical components. These studies indicate that the majority of fibers released by simulated aircraft crash-and-burn scenarios are smaller than the fibers causing electrical conductivity problems (Bell, 1980; Sussholz, 1980; NASA, 1978). A similar study of fiber release from surface vehicles utilizing graphite composites concluded that the potential risks of economic losses from accidental fiber release are relatively small. The expected national loss was estimated to be about \$5,600 per year for 1993, with the average loss per incident on the order of a few cents (Hathaway, et al., 1980).

TABLE 3-1.
PYROLYSIS PRODUCTS OF CARBON FIBERS AT 1,000°C (in Percent of Total Product)

Sample Number	Carbon Dioxide	Propane	Propene	Benzene	Toluene	Dimethyl Benzene	Naphthalene	Methyl Naphthalene
1	100	--	--	--	--	--	--	--
2	100	--	--	--	--	--	--	--
3	100	--	--	--	--	--	--	--
4	100	--	--	--	--	--	--	--
5	48	23.0	0.5	0.5	8.3	2.9	2.9	2.8
6	100	--	--	--	--	--	--	--
7	100	--	--	--	--	--	--	--
8	32	20.0	19.0	7.0	2.0	--	--	--
9	100	--	--	--	--	--	--	--
10	100	--	--	--	--	--	--	--
11	48	2.0	14.3	14.4	6.4	--	--	--

Source: Bazinet, et al., 1976

4.0 TOXICITY OF GRAPHITE FIBERS

Few data are available on the possible toxic effects of graphite fibers. Fibers that are released to the atmosphere are rarely of respirable size, except those produced during the machining of composite materials (Wagman, et al., 1979). Such small diameter fibers have been shown, in the case of asbestos, to produce acute skin and eye irritation, skin sensitization, chronic lung disease, carcinoma or mesothelioma. Reported exposures to man-made fibers in general have listed only skin and respiratory tract irritation as complaints, but the time of study of health effects of man-made fibers is insufficient to discount other possible health effects (NASA, 1978).

Graphite fiber composites have been studied for use in artificial joint implants in the human body. Consideration of the composites for such uses suggests that they are not toxic in that form.

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APPENDIX B

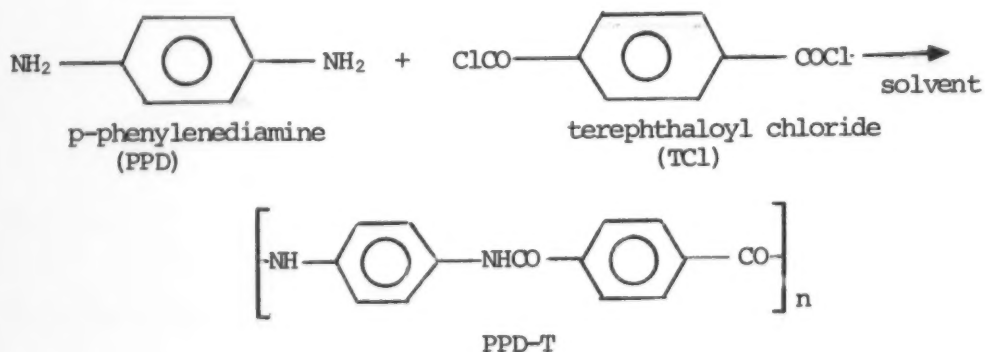
KEVLAR®

KEVLAR®

1.0 INTRODUCTION

Kevlar® is the registered trademark for one member of a group of aromatic polyamide fibers introduced by E.I. DuPont de Nemours & Co., Inc., in 1972. In 1974, the Federal Trade Commission assigned the generic term "aramid" to designate this class of manufactured fibers in which the fiber-forming substance is a long-chain synthetic polyamide with at least 85 percent of the amide ($--CO--NH--$) linkages attached directly to two aromatic rings. These polymers are formed by the reaction of aromatic diamines and aromatic diacid chlorides in an amide solvent. There is no recognized systematic nomenclature for aromatic polyamides. However, acronyms or the initial letters of the various monomers are frequently combined with the initials of the diamine moieties preceding those of the diacid moieties. The letters "T" and "I" are commonly accepted designations for terephthalamide and isophthalamine, respectively (see diagram).

A number of commercial and experimental aramids have been developed in the United States and abroad. Kevlar® and the similar Kevlar® 29 or 49 are apparently based on poly (p-phenyleneterephthalamide) (PPD-T) spun from sulfuric acid.



Kevlar® 49 is a higher modulus fiber intended for use in rigid composites, originally introduced under the experimental name of PRD-49. It is also believed to be composed of PPD-T, its higher modulus being achieved by hot drawing of the fiber (Preston, 1978). The present study will be concerned with Kevlar® 49.

The physical properties of Kevlar® 49 are shown in Table 1-1. The tensile strength of Kevlar® 49 is 400 lb/sq in which is greater than twice that of nylon or Dacron®, and almost 15 percent greater than that of E-glass. Its modulus (stiffness) of 18,000,000 lb/sq in is more than 20 times that of nylon, almost ten times that of Dacron®, and almost twice that of E-glass. Fiber elongation (strain to failure) to break is low (2.5 percent). Density (0.052 lb/cu in) is slightly higher than that of nylon or Dacron® and more than 40 percent lower than that of glass. Stress-strain curves (Preston, 1978) show Kevlar® 49 to be stronger than steel, although only one-fifth its weight. Kevlar® 49 fibers are reported to have excellent toughness, good textile processibility, and high impact strength (DuPont, 1978).

Kevlar® 49 has good thermal stability, retaining a high percentage of room temperature properties when tested up to 355°F (180°C). The fiber does not melt or support combustion but will carbonize at about 800°F (427°C). Fibers show no significant embrittlement or degradation at temperatures as low as -320°F (-196°C). Kevlar® 49 has excellent thermal dimensional stability with a slightly negative coefficient of thermal expansion of $-1.1 \times 10^{-6}/^{\circ}\text{F}$ ($-2 \times 10^{-6}/^{\circ}\text{C}$) (DuPont, 1978).

Kevlar® 49 displays excellent chemical resistance except in a few strong acids and alkalis. Fibers will lose 60 percent of their tensile strength in 70 percent HNO₃ and 100 percent in 96 percent H₂SO₄ (DuPont, 1978).

The ultraviolet resistance of aramids has practical significance. Unprotected Kevlar® has been shown to deteriorate with xenon lamp UV exposure (Sturgeon and Lacy, 1978), while very thin Kevlar® 49 fabric exposed directly to Florida sunshine loses up to half its tensile strength with time (DuPont, 1978). However, this degradation can be minimized or

prevented by the self-shielding characteristics of the fiber. In thicker ropes the majority of yarns are protected by the outer layer so that strength loss is minimal (DuPont, 1978). Multiple ply composites made with aramid reinforcements are relatively immune to UV degradation because of their thickness and the possibility of incorporating UV absorbers into the resin matrix (Sturgeon and Lacy, 1978).

The stability of composites containing Kevlar® 49 is generally good except under extremely hostile conditions. Data summarized in Table 1-2 illustrate that resin-to-fiber bonds are maintained throughout extended exposure to several typical environments. Note that the particular resin matrix employed has a significant effect on composite stability.

TABLE 1-1.
PROPERTIES OF KEVLAR® 49

	Kevlar® 49 Aramid
Tensile Strength, lb/sq in (MPa)*	400,000** (2,758)
Modulus, lb/sq in (MPa)	18,000,000 (124,110)
Elongation to Break, %	2.5
Density, lb/cu in (g/cu cm)	0.052 (1.44)
* MPa - lb/sq in x 6.895 x 10	
** Unimpregnated twisted yarn test - ASTM 02256	
*** Impregnated strand test - ASTM 02343	
From DuPont, 1978.	
Long-term use temperature in air	320°F (160°C)
Decomposition temperature	930°F (500°C)
Shrinkage	2.2 x 10 ⁻⁴ %/°F (4 x 10 ⁻⁴ %/°C)
Thermal coefficient of expansion	-1.1 x 10 ⁻⁶ in/in °F (-2 x 10 ⁻⁶ in/in °C)
Longitudinal, 0-100°C	+33 x 10 ⁻⁶ in/in °F (+59 x 10 ⁻⁶ in/in °C)
Radial, 0-100°C	
Thermal conductivity, room temperature =	
0.19 g/cu cm	
Heat flow perpendicular to fibers	0.285 = $\frac{\text{Btu} \cdot \text{in}}{\text{hr sq ft } ^\circ\text{F}}$
Heat flow parallel to fibers	0.334 = $\frac{\text{Btu} \cdot \text{in}}{\text{hr sq ft } ^\circ\text{F}}$
Specific heat, room temperature	0.34 $\frac{\text{Btu}}{\text{lb } ^\circ\text{F}}$
Heat of combustion	15,000 $\frac{\text{Btu}}{\text{lb}}$
Electron radiation	No effect
Vacuum outgassing	2.28% weight loss
Refractive index	
Parallel fiber axis	2.0
Perpendicular fiber axis	1.6
Moisture regain	3.5%
Equilibrium at 55% R.H., 72°F	
Regain rate at 55% R.H.	0.3%/hr avg.

From Sturgeon and Lacy, 1978.

TABLE 1-2.

LONG-TERM ENVIRONMENTAL STABILITY OF COMPOSITES OF KEVLAR®
 ARAMID AND FIBERGLASS
 Interlaminar Shear Strength*, lb/sq in (MPa)

Environmental Conditions	Kevlar® 49/ 250°F (121°C) Epoxy**	Kevlar®/ 350°F (177°C) Epoxy***	"S"-Glass 350°F (177°C) Epoxy***
Control	7,180 (49.5)	5,900 (40.6)	11,500 (79.2)
Boiling Water, 3-1/2 years	2,300 (15.8)	3,070 (21.2)	0
Salt Water, 3-1/2 years	4,670 (32.2)	5,900 (40.6)	11,000 (75.8)
Jet Fuel (Texaco "Abjet" K-40) 3-1/2 years	6,605 (45.5)	5,900 (40.6)	11,500 (79.2)
Lubricating Oil ("Skydrol") 3-1/2 years	6,750 (46.5)	5,900 (40.6)	11,500 (79.2)

* ASTM 02344 Short Beam Shear

** Interior Grade, General Purpose

*** Exterior Grade, High Temperature
 From DuPont, 1978.

2.0 ECONOMIC FACTORS

PRODUCTION

Product Form

Kevlar® 49 is available from DuPont in continuous filament yarns in yields from 23,000 yd/lb (134 filaments) to 3,150 yd/lb (1,000 filaments). Measurements are usually expressed in denier (weight in 9 grams per 9,000 m) or decitex (weight of 10,000 m). On this basis, yarns range from 195 denier (215 decitex) to 1,420 denier (1,580 decitex). DuPont also supplies roving in yields of 980 yd/lb (3,000 filaments) to 197 yd/lb (16,000 filaments). The basic filament for all these products has a diameter of about 0.5 mil (0.013 mm), or almost 1.5 denier per filament (1.7 decitex) (DuPont, 1978 and Smith, 1979). Yarns and roving as supplied by the manufacturer currently have no twist, but twist can be added to improve processibility (Sturgeon and Lacy, 1978).

A variety of balanced and unidirectional fabrics and roving are also available from commercial weavers, while other products such as nonwoven fabrics and felts, heavy denier pultrusion rovings, and staple fibers are under development (Sturgeon and Lacy, 1978).

Manufacturing Process

Manufacturing details for Kevlar® 49 are not available. Figure 2-1 shows the preparation of PPD-T, from which Kevlar® is spun.

In general, aramid fibers are spun directly from the polymer solution as prepared, usually in the presence of an organic or inorganic salt. Either dry- or wet-spinning techniques may be used. In the case of dry spinning, the salt remains in the spun fibers and must subsequently be leached out, as fibers containing residual salt have poorer thermal stability and electrical properties than do salt-free fibers. The yarn must be dried and is usually hot drawn whether spun by a wet or dry process (Preston, 1978).

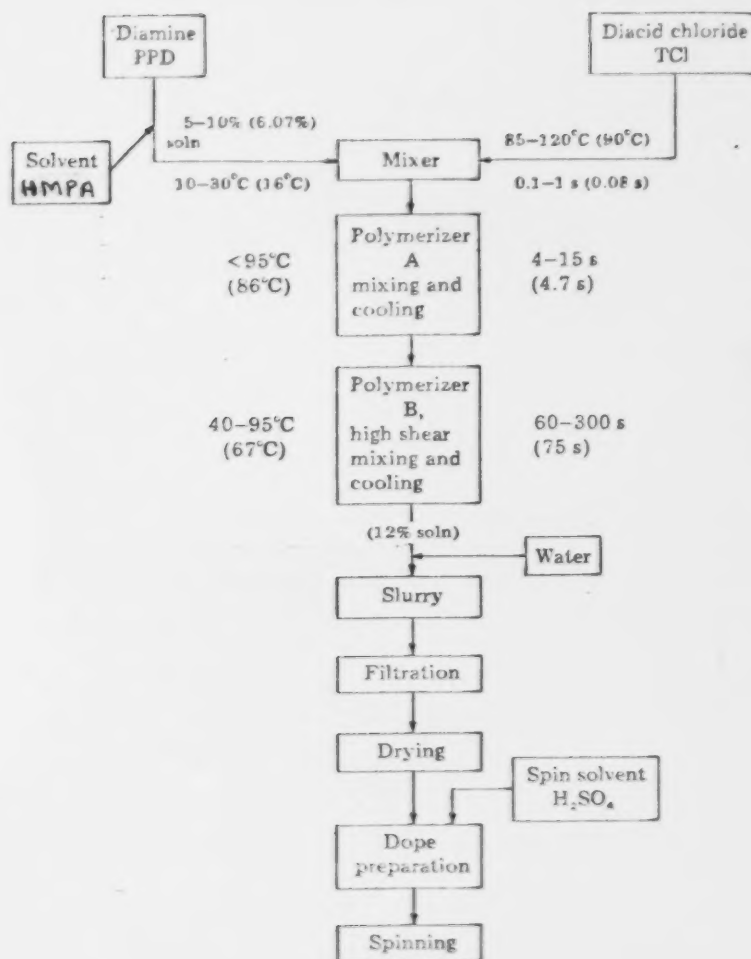


FIGURE 2-1. Preparation of PPD-T, used to spin Kevlar® fiber (6,51). Values in parentheses are from an actual example in Ref. 51; polymer of $\eta_{inh} = 5.3$ was produced.

Source: Preston, 1978.

Production Capacity

Total Kevlar® production capacity is 15 million pounds per year; it is expected to reach 45 million pounds by 1982 (Ted Lynch, Versar memo, December 30, 1980). Kevlar® 49 represents only about five to eight per cent of the total Kevlar® output (Argos, 1978). By 1990, annual total composite usage is expected to be in the millions, but not in the tens of millions, of pounds (Lynch memo, 1980).

Price

Kevlar® 49 was first offered commercially in January, 1972, at a price of \$50 per pound. Late in 1972, the price was reduced to under \$20 for some items (Sturgeon and Lacy, 1978). The current price is from \$10.50 to \$35, depending on denier. This price is not expected to come down, but will probably track inflation (Lynch memo, 1980).

CONSUMPTION

The present market for Kevlar® 49 is distributed as follows: aerospace and aircraft, 40 percent; boats and marine applications, 40 percent; and miscellaneous, 20 percent (Argos, 1978).

Aircraft

Composites of Kevlar® 49 are currently being used in non- and semi-structural aircraft components, where a weight savings of 65 to 80 percent over metals permits increased payloads and range or reduced fuel requirements.

The first major use of Kevlar® in aircraft was in Lockheed's L-1011 Tri-Star. Twelve hundred pounds (590 kg) of Kevlar® composite materials were used in both interior and exterior parts, including window reveals, overhead storage bins, ceiling panels, instrument panels and consoles, wing-to-body fairings, wing leading and trailing edges, access panels, pylons, and nacelles (DuPont "Weight," Watts, 1980).

The DeHavilland Dash 7 makes extensive use of Kevlar® in the cabin interior, as well as externally in the nose avionics compartment, leading edge of leading flap, and various aerodynamic fairings (John and Bryson, 1978; John, 1980).

Cessna uses Kevlar® externally in its Citation 3 business jet and in its Conquest 441. In the Conquest 402, Kevlar® composites have replaced steel in the passenger seats (North, 1979). Canadair's wide-body business jet, the Challenger, will use Kevlar® in landing gear doors, instrument panels, radome, air ducts, wheel bins, and consoles (DuPont "Weight").

Kevlar® composite propeller blades developed by Hartzell Propeller, Inc., are reported to be highly efficient and quiet at a reasonable weight, taking less time to manufacture and requiring fewer repairs (Harlamert and Edlinger, 1979; North, 1979). A Spanish Casa 212 has been outfitted with the first set of the new blades (DuPont "Weight").

Kevlar® has also found use in helicopters. The Sikorsky S-76 commercial helicopter contains 138 internal and 25 external parts of Kevlar®, including the nose section, cockpit canopy, all upper deck fairings, horizontal stabilizer, coor, pylon, and floor ("Mustered," DuPont "Weight"). Sikorsky's Blackhawk army helicopter uses Kevlar® in the fairings, doors, access panels, and instrument panels, as well as for ballistic armor in the cockpit seats (DuPont "Weight").

Composites are used extensively in helicopter blades. Most are now hybrid systems composed of fiberglass selectively reinforced with aramid or graphite fibers. Kevlar® is used in the main rotor blades of the Blackhawk and CH-46 models. Hughes Aircraft has developed a unidirectional aramid composite blade which may go into production (Argos, 1978).

Other Kevlar® uses in aircraft include fuselage skins, engine cowls, cargo liner panels, partitions, lavatories, galleys, and bulkheads, as well as pressure bottles used to activate escape slides and life rafts (DuPont "Weight"; DuPont, 1978, Wehrenberg, 1980a). Kevlar® composites are also being evaluated for additional uses, such as jet engine blade containment, cargo containers, restraint webbing, escape slides and life rafts, circuit boards, and as acoustical insulation for engines (DuPont "Weight").

Rockets and Missiles

Lightweight composites are essential in the construction of rockets and missiles, where 20 pounds of fuel and engine are required to lift one pound of payload off the ground (Wehrenberg, 1980a). Kevlar® is used in filament wound pressure vessels and solid rocket motor cases as well as in launch tube reinforcement. For example, rocket engine cases of all three stages of the Trident C-4 ICBM are fabricated with filament wound Kevlar® 49 composite (DuPont "Weight," Watts, 1980).

The space shuttle Orbiter built for NASA by Rockwell Industries Space Division contains thousands of pounds of composites including Kevlar®/epoxy overwraps for the 17 spherical metal-lined pressure vessels storing liquid oxygen and nitrogen. Kevlar® is also used in the shuttle for lightweight ducting for the purge, vent, and drain system (Watts, 1980).

Marine Applications

Composites reinforced with aramids provide lighter, stiffer, more damage tolerant and vibration damping laminates for marine applications than do composites reinforced with glass fibers. Therefore, Kevlar® is used to reinforce the hulls, decks, and bulkheads of many types of boats. The most cost effective aramid laminates are those including glass fibers in combination form and using polyester resin matrices (Norwood and Marchant, 1980). DuPont estimates that water craft will ultimately use 20,000 tons per year of advanced composites ("Composites," 1979).

Kevlar® has been shown to be cost effective in fishing boats saving in operating costs over the years (Stearns, 1978, 1979). Eight bass boat manufacturers offer aramid fibers as an option, and Hydra-Sports of Nashville, Tennessee, reports that more than 90 percent of their 1977 orders were for boats built with Kevlar®. A boat of Kevlar® holds the world's speed record for bass boats - 80.214 mph (Alegranti, 1978). Hydra-Sports also manufactures offshore fishing boats with Kevlar® hulls ("Hydra-Sports").

More than 40 canoe and kayak manufacturers now offer models with Kevlar® 49 and Kevlar® is used to fabricate about 80 percent of canoes and kayaks that engage in downriver and slalom competition (Alegranti, 1978; Watts, 1980).

Kevlar® is used extensively in power racing boats, and all key manufacturers of offshore racing boats now use Kevlar® exclusively for serious entries to the unlimited class (Alegranti, 1978). It is also used in the manufacture of power boats for other types of racing events including Grand National boats, outboard tunnel hulls, and river racing (Watts, 1980).

Kevlar® utilization in sailboats is fairly limited. Moreover, racing rules often prohibit or restrict its use in spars. This does not, however, affect the use of composites in hull design (Argos, 1978; Watts, 1980).

Several prototypes for Coast Guard and military patrol boats utilizing Kevlar® are in building/testing stages (Alegranti, 1978).

Sporting Goods

Kevlar® 49 is also being used successfully in a number of sporting goods items. In hockey sticks, Kevlar® can be either laminated directly to wood or combined with glass fibers in an all-composite stick. Kevlar® 49 is used in combination with graphite in golf shafts, javelins, archery bows, fishing rods, tennis rackets, and skis (DuPont, 1978). It is also used in arrows, bows and paddles, surfboards, and helmets (Watts, 1980).

Minor Uses

Kevlar® 49 composites have been evaluated for automotive applications. For example, Budd Company has developed a graphite/aramid/epoxy transmission support. Kevlar® hybrids have also been developed for driveshafts, humpers, leaf springs, radiator supports, wheels, and body parts. Nevertheless, Kevlar's® potential in this area is limited, with graphite the reinforcing material of choice (Watts, 1980; Wehrenberg, 1980b).

Kevlar® 49 is replacing steel in tension members and cables, especially very long cables such as those in oceanographic and aerospace markets (DuPont, 1978; DuPont "Properties").

Fabrics of Kevlar® 49 are used as load-bearing substrates in a variety of coated fabric applications, such as in architectural fabrics, inflatable life rafts and escape slides, portable storage tanks, and nonstick conveyor belting (DuPont, 1978).

Projected Uses

Used with low shear strength polyester or phenolic resins, Kevlar® 49 may be used to produce hard armor capable of resisting damage caused by ballistic impact. It is now being evaluated for use in aircraft and helicopter components, infantry helmets, shipboard armor, armored cars, and jet engine blade containment (Watts, 1980).

Kevlar® 49 is also being evaluated as a safe replacement for asbestos in friction products such as clutch plates and brake linings (Watts, 1980; Loken, 1980).

Other potential uses for Kevlar® 49 composites include space structures, primary structures on aircraft and helicopters, industrial equipment, energy generating devices, flywheels, civil engineering structures, musical instruments, and speaker cones (Sturgeon and Lacy, 1978; Watts, 1980).

3.0 ENVIRONMENTAL

See Section 1.0 for data on environmental stability. No data are available on Kevlar® environmental fates or degradation products per se.

4.0 TOXICITY/BIOCHEMISTRY

No evidence of skin sensitization was found when Kevlar was tested on guinea pig skin under occluded conditions or in a 200-subject prophetic patch test on human skin. No skin irritation was found after 48 hours of continuous contact. Some irritation, probably from mechanical causes, did occur after 144 hours of continuous occluded contact (DuPont, 1979).

Some processing operations might generate fly. However, the material which may be seen is expected to fall out and not remain airborne, and is outside the range considered respirable. DuPont has concluded that:

1. Concentration of elongated particles and total dust were low compared to existing standards for nuisance and allergenic dust, and were in the range of standards for fibrogenic dust and,

2. Based on animal insufflation tests, respirable dust from Kevlar® produced what would be considered a typical lung reaction to a nuisance dust particulate (DuPont, 1979).

No further toxicological data on Kevlar® itself is available. It should be pointed out that the manufacture of reinforced plastics involves the handling of dozens of resins, solvents, curing agents, accelerators, thixotropic agents, etc., each with its own potential hazard (Sturgeon and Lacy, 1978). Laboratory vapor inhalation tests have indicated that one of the in-process solvents, hexamethylphosphoramide (HMPA) used in Kevlar® manufacture, will produce cancer in rats (Zapp, 1975). There is no evidence that this solvent or its vapor has caused cancer in humans. In any case, any residual HMPA that may be retained by Kevlar® after processing is reportedly too tightly bound to the fiber to present a serious inhalation problem (Sturgeon and Lacy, 1978; Preston, 1978).

The combustion products of Kevlar® were determined in 1976 in a series of fast and slow pyrolysis experiments (Bazinet, *et al.*, 1976). Fast pyrolysis in a 650°C furnace produced approximately 63 percent carbon monoxide, 35 percent benzene, and 2 percent toluene. Slow pyrolysis produced at least 15 compounds and a series of nitrogen-containing cyclic

compounds. These included nitrogen, carbon monoxide, carbon dioxide, methane, ethylene, propene, benzene, toluene, benzonitrile, aniline, methylaniline, phenylacetone, phthalonitrile, phenyldiamine, biphenyl, benzimidazole, fluorene, and benzanilide. No ammonia or hydrogen cyanide were observed. No trace of residual HMPA was observed at sensitivities down to 1 ppm.

Tatem and Williams (1980) studied the combustion pyrolysis profiles of Kevlar® and a Kevlar®-resin system under three types of thermal stress: direct flame impingement under atmospheric oxygen, and thermal radiation under both atmospheric (21 percent) and low (10 percent) oxygen conditions. The two sample types were a Kevlar® blanket and a Kevlar® plus Derakane® 510 resin system. The main gaseous products identified were aliphatic and aromatic hydrocarbons.

The three stresses were chosen to encompass several conditions that might exist in an actual fire. Kevlar® began to degrade at 475°C. The oxygen concentration at and beyond this point has an effect on the nature of the combustion products evolved. It may be possible for Kevlar® to be exposed to heat from a fire but not directly to flames in an environment with reduced oxygen concentration; in the case of a fire under reduced or nonexistent ventilation, atmospheric oxygen can be rapidly consumed resulting in oxygen-deficient combustion. Tables 4-1 and 4-2 show the products of combustion under the different conditions of the experiment.

The products acrolein, styrene, and ethylbenzene were produced only by the Kevlar®-resin system. The high yields of styrene and ethylbenzene are not surprising, since Derakane® 510 is a vinyl ester containing 40 percent styrene. The "worst case" for the system in terms of the quantity of these chemicals released is represented by thermal degradation at 21 percent oxygen. Acrolein is highly toxic (lethal in a short time at concentrations as low as 10 ppm), but is a lachrymator and will serve as its own warning agent. Trace amounts of propionitrile were liberated by the system under 10 percent oxygen; the highly toxic effects of this compound are intensified by its ability to be absorbed through the skin.

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TABLE 4-1
CHEMICAL COMPOUNDS GENERATED FROM EXPOSURE OF KEVIAR® +
DERAKANE® 510 RESIN SYSTEM TO VARIOUS STRESSES

Compound	Peak No.**	Structure	Mg of Product/Gram of Sample Consumed*		
			10% Oxygen Thermal	21% Oxygen Thermal	Hydrogen Torch
Methane	1	CH ₄	0.36	1.3	0.67
Unknown	2	---	---	---	---
Ethene	3	CH ₂ =CH ₂	0.27	1.1	0.58
Acetylene	4	HC≡CH	0.01	0.02	3.0
Ethane	5	CH ₃ -CH ₃	0.04	0.19	---
Propene	6	CH ₂ =CH-CH ₃	0.8	3.2	0.02
Propane	7	CH ₃ -CH ₂ -CH ₃	+	+	+
Unknown	8	---	+	+	+
Unknown	9	---	+	+	+
Unknown++	10	---	0.65	2.4	---
1-Butene	11	CH ₂ =CH=CH ₂ CH ₃	0.62	1.8	---
Butane	12	CH ₃ (CH ₂) ₂ CH ₃	---	---	---
Unknown	13	---	---	---	---
Acetonitrile	14	CH ₃ CN	+	+	0.01
Acrolein	15	CH ₂ =CHCHO	1.7	4.5	+
1-Pentene	16	CH ₂ =CH(CH ₂) ₂ CH ₃	0.53	1.8	---
Acetone	17	CH ₃ COCH ₃	1.5	5.9	0.06
Pentane	18	CH ₃ (CH ₂) ₃ CH ₃	+	+	+
Unknown	19	---	+	---	---
Unknown	20	---	+	---	---
Propionitrile	21	CH ₃ -CH ₂ CN	+	---	---
2-Hexene	22	CH ₂ =CH(CH ₂) ₃ CH ₃	+	+	---
Hexane	23	CH ₃ (CH ₂) ₄ CH ₃	+	+	---
Unknown	24	---	+	---	---
Unknown	25	---	+	+	---
Benzene	26	C ₆ H ₆	0.07	0.95	1.2
Unknown	27	---	+	+	---
Unknown	28	---	+	+	---
Toluene	29	C ₆ H ₅ CH ₃	0.91	6.2	0.07
Ethyl benzene	30	C ₆ H ₅ CH ₂ CH ₃	1.5	6.6	0.46
Styrene	31	C ₆ H ₅ CH=CH ₂	52	108	44
Unknown	32	---	+	+	+
Unknown	33	---	+	+	+

* HCL and HCN analyses are accurate to within 20%; all other analyses to within 5%.

** Peak numbers refer to chromatograms in Figures 2 and 3.

--- Absent

+ Present but <0.01 mg/g

++ Calculated as 1-butane equivalents

Source: Tatem and Williams, 1979

TABLE 4-2
CHEMICAL COMPOUNDS GENERATED FROM EXPOSURE OF KEVLAR®
BLANKET TO VARIOUS STRESSES

Compound	Peak No.	Structure	Mg of Product/Gram of Sample Consumed*		
			10% Oxygen Thermal	21% Oxygen Thermal	Hydrogen Torch
Methane	1	CH ₄	0.06	0.19	0.58
Unknown	2	—	—	—	+
Ethene	3	CH ₂ =CH ₂	0.09	0.21	0.38
Acetylene	4	HCECH	—	+	0.32
Ethane	5	CH ₃ -CH ₃	+	0.01	0.03
Propene	6	CH ₂ =CH-CH ₃	0.02	0.07	0.10
Propane	7	CH ₃ -CH ₂ -CH ₃	+	+	0.10
Unknown	8	—	+	+	+
Unknown	9	—	—	+	+
Unknown++	10	—	0.38	0.82	0.07
1-Butene	11	CH ₂ =CH=CH ₂ CH ₃	0.34	0.60	0.07
n-Butane	12	CH ₃ (CH ₂) ₂ CH ₃	+	+	0.04
Unknown	13	—	+	+	+
Acetonitrile	14	CH ₃ CN	—	0.04	0.48
Acrolein	15	CH ₂ =CHCHO	—	—	—
1-Pentene	16	CH ₂ =CH(CH ₂) ₂ CH ₃	0.13	0.42	0.01
Acetone	17	CH ₃ COCH ₃	+	0.45	0.08
Pentane	18	CH ₃ (CH ₂) ₃ CH ₃	+	0.02	0.07
Unknown	19	—	—	—	—
Unknown	20	—	—	—	—
Propionitrile	21	CH ₃ -CH ₂ CN	—	—	—
2-Hexene	22	CH ₂ =CH(CH ₂) ₃ CH ₃	0.01	0.02	0.01
Hexane	23	CH ₃ (CH ₂) ₄ CH ₃	0.01	0.02	0.01
Unknown	24	—	—	—	—
Unknown	25	—	—	—	—
Benzene	26	C ₆ H ₆	—	0.03	4.4
Unknown	27	—	—	+	+
Unknown	28	—	—	+	+
Toluene	29	C ₆ H ₅ -CH ₃	—	0.19	0.42
Ethyl benzene	30	C ₆ H ₅ -CH ₂ CH ₃	—	—	—
Styrene	31	C ₆ H ₅ CH=CH ₂	—	—	—
Unknown	32	—	—	+	+
Unknown	33	—	—	+	+
Unknown	34	—	—	+	+
Hydrogen Chloride		HCl	—	—	0.08
Hydrogen Cyanide		HCN	—	—	0.10
Carbon Dioxide		CO ₂	22	21	980
Carbon Monoxide		CO	2.1	10	25

* HCL and HCN analyses are accurate to within 20%; all other analyses to within 5%.

-- Absent

+ Present but <0.01 mg/g

++ Calculated as 1-butane equivalents

Source: Tatem and Williams, 1979

Small amounts of hydrogen cyanide and hydrogen chloride were released from Kevlar® alone under direct flame impingement.

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APPENDIX C
SILICON CARBIDE

SILICON CARBIDE FIBERS

1.0 INTRODUCTION

Silicon carbide (SiC) fibers are available in the form of continuous filaments and whiskers. Continuous SiC filaments were originally developed by General Technologies Corporation under a 1966 contract to the U.S. Air Force Materials Laboratory. The filaments are produced using a chemical vapor deposition process in which SiC is deposited on either tungsten filament or carbon filament cores with the carbon filament process being relatively new. SiC filament was developed to fill the needs of the metal matrix composite industry. Boron filament rapidly lose strength at temperatures above 1,000°F and is therefore not suitable for high temperature applications. In addition, boron reacts with molten metals, such as aluminum, making the fabrication of metal matrix composites through liquid metal infiltration a standard casting technique not feasible. In contrast, SiC filaments retain their strength at temperatures well beyond 1,000°F and can withstand exposure to molten aluminum.

2.0 ECONOMIC CONSIDERATIONS

PRODUCTION (CONTINUOUS FILAMENT)

Silicon carbide filaments are produced in continuous form by decomposition of methylchlorosilanes on a heated substrate in the presence of hydrogen. The substrate may be tungsten or carbon. The deposition rate of SiC is high relative to its sister material boron. This is a result of its higher specific gravity (3.1) versus (2.4) for boron, and due to a faster rate of deposition. It is estimated that a single reactor can produce 150 pounds per year of silicon carbide versus 90 pounds per year of boron from the same reactor.¹

The principal raw materials for the production of silicon carbide fibers are methylchlorosilanes, hydrogen gas, and tungsten or carbon filament. Methyl chlorosilanes are common chemicals currently needed to make silicones and organic silanes. The price of methyl dichlorosilane is

is about \$1 per pound. Approximately five pounds of methyl dichlorosilane is required to produce a pound of silicon carbide. Although there is not theoretical requirement for hydrogen in the production of silicon carbide, the product produced using hydrogen shows much improved quality versus that produced without hydrogen. Approximately 60 kwh of electricity are needed per pound of silicon carbide fiber. A breakdown of production costs is depicted in Tables 2-1 and 2-2.¹

Avco Corporation in Lowell, Massachusetts, is the sole U.S. producer of continuous silicon carbide filament. A similar material is being produced in small quantities in West Germany by the Berghof Research Institute, which is represented in the United States by Fiber Materials, Inc. of Biddeford, Maine. A totally different filament produced from a polymeric starting material is being developed in Japan by Nippon Carbon. Presently the properties of this material are far inferior to the Avco and Berghof materials.

PRODUCTION (WHISKERS)

Silicon carbide whiskers can be produced by either of two ways. The techniques include (1) the vapor deposition process and (2) a recently developed process whereby rice hulls are pyrolyzed to product silicon carbide. Whiskers grown using the vapor deposition technique are of the higher quality but are considerably more expensive to produce. In this process a whisker is grown by a vapor-liquid-solid mechanism. A gaseous mixture of hydrogen, carbon monoxide, methane, and nitrogen is passed through a reactor containing a silica source. The reactor temperature can vary between 2,300°F and 2,800°F² with growth times ranging from 4 to 24 hours. SiO is generated by reducing silicate-containing insulating brick within the reactor. Carbon monoxide and methane are added directly to the reactor. The methane is cracked in the reactor into acetylenic-free radicals and serves as a carbon donor. Metal powders are painted on the graphite surfaces of the reacrod modules so as to act as nucleation sites. Stainless steel and iron powder are commonly used.

The rice hull pyrolysis process has many advantages over the vapor deposition process. The primary advantage is the economics of the

TABLE 2-1
PROJECTED LOW VOLUME MANUFACTURING COSTS OF 5.6 MIL SILICON CARBIDE
FILAMENTS ON A TUNGSTEN SUBSTRATE

Production Rate, lbs/year (kg/yr)	15,000 (7,000)
Capital Investment, \$10 ⁶	2.0

<u>OPERATING COSTS</u>			
<u>Item</u>	<u>Units/lb SiC</u>	<u>Unit Cost</u>	<u>Cost/\$1b SiC</u>
Methyltrichlorosilane	5.0/lb	\$0.80/lb*	\$4.00
Hydrogen	600 SCF	\$11/SCF	6.00
Tungsten substrate	30,000 ft	\$2.50/10 ³ M	23.00
Other chemicals and supplies			2.00
Electric power	60 kwh	\$0.04/kwh	<u>2.40</u>
Subtotal Materials and Energy			\$37.40
Direct labor	0.6 manhour	\$8/manhour	4.80
Overhead and supervision	100% direct labor		<u>4.80</u>
Subtotal labor and supervision			\$9.60
Depreciation (5 years)			27.70
Interest, 10% capital investment/year			13.80
Maintenance, 6% capital investment/year			<u>8.00</u>
Subtotal capital related charges			\$49.00
Total Operating Costs			\$96.00

* Assumed.

TABLE 2-2
PROJECTED HIGH VOLUME MANUFACTURING COSTS OF 5.6 MIL SILICON CARBIDE
FILAMENTS ON A CARBON SUBSTRATE

Production Rate, lbs/year, 10^6

Capital Investment, $\$10^6$

<u>Item</u>	<u>OPERATING COSTS</u>		
	<u>Units/lb SiC</u>	<u>Unit Cost</u>	<u>Cost/\$lb SiC</u>
Methyltrichlorosilane	5.0/lb	\$0.80/lb*	\$4.00
Hydrogen	Trace		--
Carbon substrate	0.08/lbft	\$30/lb	2.40
Other chemicals and supplies			2.00
Electric power	60 kwh	\$0.04/kwh	<u>2.40</u>
Subtotal Materials and Energy			\$10.80
Direct labor	0.3 manhour	\$8/manhour	2.40
Overhead and supervision	100% direct labor		<u>2.40</u>
Subtotal labor and supervision			\$4.80
Depreciation (5 years)			6.00
Interest, 10% capital investment/year			3.00
Maintenance, 6% capital investment/year			<u>1.80</u>
Subtotal capital related charges			\$10.80
Total Operating Costs			\$26.40

* Assumed.

production process. Presently the sole producer of rice hull silicon carbide, Exxon Enterprises, is charging \$95 per pound of whisker while the price of vapor deposited silicon carbide is approximately \$10,000 per pound. Presently, this process generates 15 pounds of silicon carbide from 100 pounds of rice hulls. Twenty-five percent or 3.75 pounds of the SiC is whiskers approximately 1 micron to 3 microns in diameter and with length to diameter ratios of over 10. In 1980, 2,000 pounds of silicon carbide whisker was produced by Exxon. The 1981 production should reach 7,000 pounds.³

The vapor deposition whiskers are available at Versar Inc. of Springfield, Virginia, while the rice hull material is produced by Exxon in Greenville, South Carolina.

CONSUMPTION

Presently the usage of silicon carbide fibers and whiskers is very limited. In 1980, U.S. consumption of the continuous filament was only about 200 pounds. Due to the economics of silicon carbide over boron and the similarity of mechanical properties (Table 2-3), silicon carbide is expected to displace much of the boron presently in use and even displace some graphite filament. Avco projects the 1900 silicon carbide market to be 50 to 100,000 pounds per year. The major "new" market for silicon carbide filament will be as a reinforcement member of metal matrix composites.

TABLE 2-3
MECHANICAL PROPERTIES DATA FOR SILICON CARBIDE/2024 aluminum - T4⁴

	Percent Volume Fraction Silicon Carbide		
	15	20	25
UTS, Ks:	58-63	66-76	80-93
E, Ms:	13-14	14-17	17-22
UCS, Ks:	---	80-100	---

Continuous filament silicon carbide/aluminum composites exhibit very good properties when prepared using diffusion bonding fabrication techniques. A good deal of activity has been pursued to develop the capability to wet silicon carbide with molten aluminum and then produce wire as in graphite/aluminum wire production, or to develop the ability to cast silicon carbide/aluminum parts. There is a great deal of interest in silicon carbide/titanium composites for aircraft engine applications as well as a means of reducing the overall usage of titanium which is considered to be a critical material. This reduction could come about as a result of enhancing the properties of titanium and thereby reducing the mass of material required to give a body the desired structural properties. Applications for silicon carbide/aluminum are projected to include: Army bridging, Navy hydrospace structures, and Navy ordnance.

Silicon carbide whiskers open up vast new avenues to silicon carbide metal matrix composites. The principal reason for this is the fact that most powder metallurgy manufacturing technology can be utilized to produce finished components. This plus the fact that the price of whiskers is projected to reach \$5 to \$15 per pound by the late 1980's will yield an ability to produce parts which show good mechanical properties (Table 2-3) at relatively low prices. To date parts have not been pressed, extruded, rolled, and hot isostatic pressed.

POSSIBLE ALTERNATIVES

Recently DWA Composite Specialties Inc. unveiled the results of work they pursued in developing aluminum reinforced with silicon carbide particulate. The incentive was to see if a low cost (approximately \$5 per pound) commercially available material such as this would produce an enhanced aluminum. To date the results have been dramatic. Tensile moduli of 16 to 25 million have been achieved and tensile strengths in excess of 100 Ks are achievable. This material is presently being investigated by the Air Force, the Marines, and the Defense Advanced Research Projects Agency. Parts have been fabricated using diffusion bonding, extrusion, and forging. The present capacity for this material is 25,000 to 30,000 pounds per year. This should be increased to 50,000 pounds in 1981 depending on demand. In

the future, the capacity is virtually unlimited since it requires conventional equipment already in widespread use. The present price of the material is \$100 per pound of composite. This figure is expected to drop to \$50 per pound by the end of 1981 and eventually hit \$10 per pound.

3.0 ENVIRONMENTAL CONSIDERATIONS

Silicon carbide is a very stable, relatively inert material. Most reactions occur only at high temperature (Table 3-1). Potential for breakdown and leachate formation under normal environmental conditions is extremely small. However, data on this are not available.

DISPOSAL METHODS

Silicon carbide decomposes at extremely high temperatures, somewhere between 2,250°C and 2,500°C, into silicon vapor and graphite. Ordinary combustion processes will have little or no effect on silicon carbide and, therefore, can not be used as a disposal technique. Landfilling appear to be the only viable disposal technique.

RECYCLING

No information on recycling of silicon carbide was located. The economics of recycling are questionable both in the case of whiskers and for continuous filament. Whiskers recovered through the thermal removal of the metal matrix are of such low quality that there is little incentive to recycle. In the case of continuous filament, short filaments sized to the part to be recycled would be recovered and no longer truly continuous. This would seem to remove the incentive to recycle.

4.0 TOXICITY

Data are not readily available to assess the toxicity of silicon carbide filaments and whiskers. The chemical inertness of silicon carbide would seem to rule out toxicity as a problem.

TABLE 3-1
REACTION OF SILICON CARBIDE

<u>Reagent</u>	<u>Temperature</u>	<u>Reaction</u>
Hydrochloric acid	Boiling	None
Hydrofluoric acid	Boiling	None
Sulfuric acid	Boiling	None
Fuming nitric acid	Hot	None
Oxyhydroben blast	Fused	Slow oxidation
Air	1,000°C	Slow oxidation
Lead chromate	Fused	Slow oxidation
Calcium oxide	1,000°C	Is attached
Magnesium oxide	1,000°C	Is attached
Sodium silicate	1,300°C	Is attached
Potassium carbonate	Fused	Decomposes
Alkali sulfates	Fused	Decomposes
Borax	Fused	Decomposes
Cyrolite	Fused	Decomposes
Potassium hydroxide	900°C	Forms silicon tetra- chloride and carbon
Copper oxide	800°C	Forms metal silicide

The small size of the whiskers, 1 micron to 3 microns in diameter, could possibly lead to respiratory problems based upon studies of asbestos fibers, but the fibers in normal use are firmly encased in a matrix which should not break down.

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APPENDIX D
GLASS FIBERS

GLASS FIBERS

1.0 INTRODUCTION

Glass fibers used as reinforcement in resin matrices vary in grade; for the purposes of this discussion, only fibers designated "E" or "S", or better, comprise advanced composites. The chemical composition of these fibers is depicted in Table 1-1. It is assumed that all fibrous glass used in automotive and aerospace applications is E- or S-glass. Glass fibers may also be used in conjunction with other reinforcement, such as aramid or graphite, in "hybrid" advanced composites.

E-glass, generally known as a glass reinforcement fiber, is lower in tensile strength and modulus than S-glass. The properties of each type are summarized in Table 1-2. The high strength and thermal stability of glass fiber composites make them attractive for advanced applications.

2.0 ECONOMIC FACTORS

2.1 PRODUCTION

2.1.1 U.S. Production

Five major manufacturers produce glass fibers for reinforcement: Owens-Corning, PPG Industries, Certain Teed, Reichold, and Johns-Manville. Figure 2-1 illustrates total production of glass reinforcement fibers in the United States, with projections through 1985. Data are insufficient to determine the market share of each manufacturer, or to determine exactly what proportion of total fiber production is E- or S-glass.

2.1.2 World Production

No data are available on production of glass fibers outside the United States.

2.1.3 Production Methods

Figure 2-2 illustrates the general production of glass fibers.

TABLE 1-1
GLASS FIBER CHEMICAL COMPOSITION

	Percent by Weight	
	<u>E glass</u>	<u>S Glass</u>
SiO ₂	54	65
Al ₂ O ₃	14	25
B ₂ O ₃	10	10
MgO	4.5	--
CaO	17.5	--

TABLE 1-2
PROPERTIES OF GLASS FIBERS USED IN ADVANCED COMPOSITES

<u>Type of Glass</u>	<u>Density, g/cm</u>	<u>Tensile Strength, psi</u>	<u>Modulus, psi</u>	<u>Thermal Expansivity x 10⁻</u>
E	2.54	400-500 x 10	10.5 x 10	60
S	2.49	650 to 700 x 10	12.5 x 10	34

<u>Type of Glass</u>	<u>Annealing pt, °C</u>	<u>Refractive Index</u>
E	715	1.541
S	970	1.523

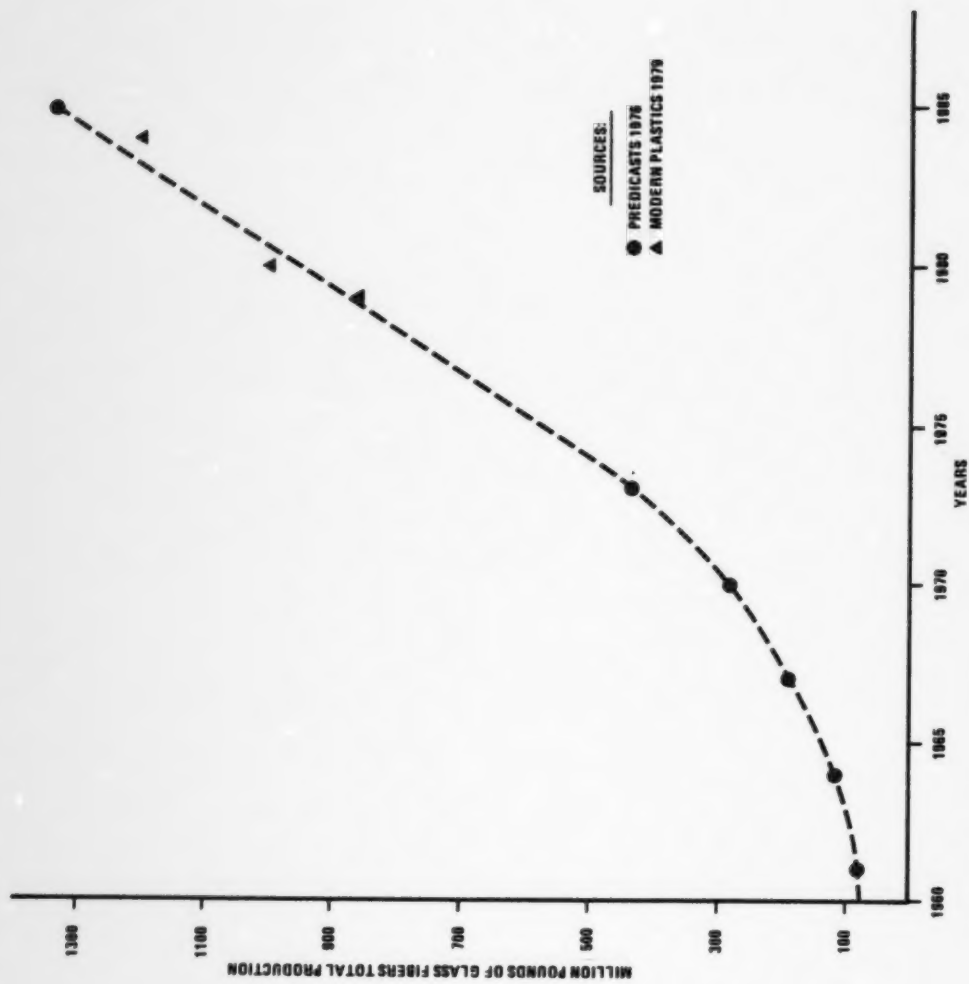
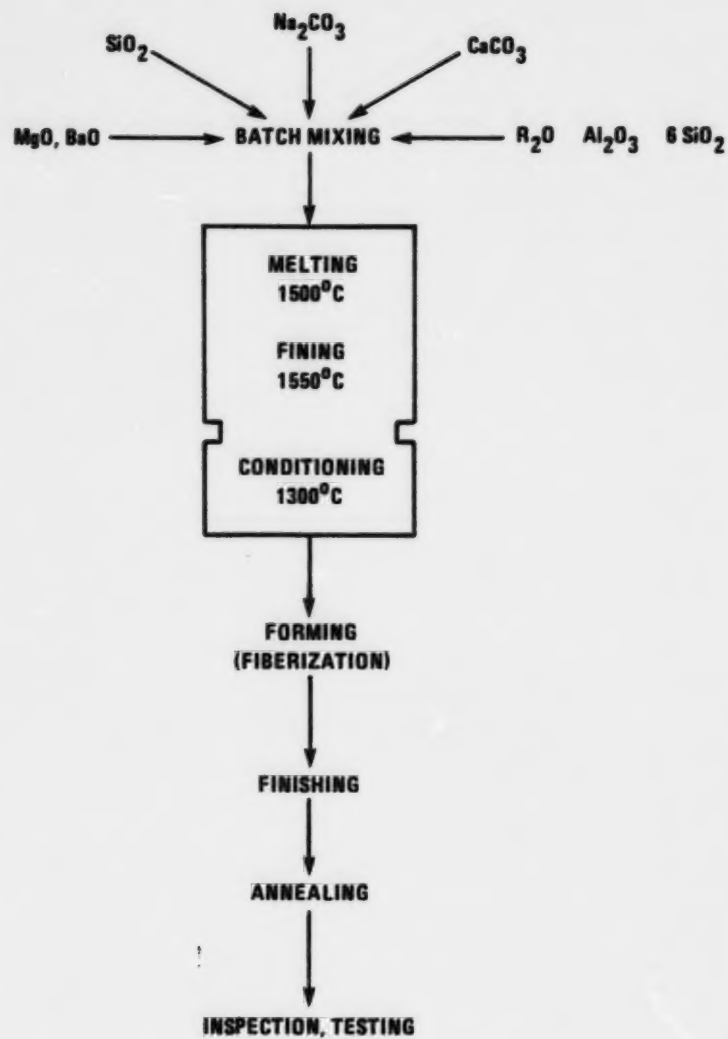


FIGURE 2-1. TOTAL PRODUCTION OF GLASS FIBERS FOR PLASTICS REINFORCEMENT



SOURCE: KIRK-OTHMER 1980

FIGURE 2-2. MANUFACTURE OF GLASS FIBERS

Fibers are formed from the molten glass by drawing the mass through air or molten tin (Kirk-Othmer 1980). The grade of glass may be varied by addition of various oxides to the batch mixture; the use of BeO and other rare-earth metal oxides results in a higher strength, higher modulus product, though at some greater cost (Bacon 1976, Galasso 1969). These higher grade glass fibers are not currently produced in commercial quantities.

After formation, the glass fibers may be chopped, woven, or wound into strands of continuous filament. Various processes are used to combine the fiber with the resin matrix, usually at a ratio of 68:32 for matrix: fiber (Galasso 1969).

2.2 CONSUMPTION

2.2.1 Applications

- Automotive

Current uses of composites in automobile manufacturing are restricted to fiberglass reinforced plastics. The best known application of composites in the auto industry is the Chevrolet Corvette. Since its introduction in the mid-1950's the Corvette's exterior body has been fabricated by compressive molding of SMC.

The 1979-80 models of U.S. cars utilize about 190 pounds of plastics per car on the average and about 10 percent or about 20 pounds of this total are fiber reinforced plastics. The 1979 cars and trucks utilized 628 different fiberglass reinforced plastic parts; 237 body panels, 217 under the hood, 93 in the passenger compartment, 61 electrical, and 20 in engine drive systems. Some of these applications are listed below:

Body Panel and Exterior Components

Air deflectors
Body pillar
Fender extension
Fender lines
Grille opening panels
Tilt front ends (truck)
Rear quarter panels
Window mechanism

Interior

Bench seats
Floor consoles
Instrument panels and parts
Bucket seats
Steering column covers
Structural supports

Under Hood

Air conditioner housing and parts
Battery trays and retainer parts
Brake cylinder
Fan blade
Oil suction tube
Fan shroud

Engine Drive Systems

Transmission parts
Clutch release lever

Electrical

Coil bobbins
Computer housings
Distributor cap and parts
Ignition housings
Junction boxes
Lamp sockets

Most of these applications are for nonload-bearing parts, but a major load-bearing application is being introduced in the 1981 Chevrolet Corvette. An eight-pound single leaf transverse rear spring made from fiberglass reinforced epoxy is used to support up to 3,500 pounds of static and dynamic load. This single composite part replaces a 45-pound multi-leaf steel spring and tests indicate that it is more durable than the steel unit. Considerable effort has been expended in the development of fiberglass epoxy driveshafts produced by filament winding techniques. The trend towards front wheel drive has diminished the potential for composite driveshaft applications in the passenger car but such applications in trucks are expected in the near future.

● Marine

The use of fiber reinforced plastics in the marine industry amounted to almost 20 percent of the total reinforced plastics production in 1979 and is second only to the automotive industry in terms of production quantities. Fiberglass pleasure boat production comprises almost 60 percent of the total pleasure boat market. Commercial craft also continue to convert to reinforced plastics for hulls and decks, and for the same reasons - strength, light weight, durability, corrosion resistance, and easy maintenance.

● Aircraft and Aerospace

Fiberglass reinforced plastics have a multiplicity of nonstructural and semi-structural applications in commercial aircraft. The energy crunch has broadened the interest in composite applications and intensified

efforts to utilize the advanced fibers in new applications or to replace glass fiber in current applications. The progress has been slow partly due to costs and fabrication technology and partly due to FAA certification requirements, but progress is being made.

● Consumer Goods

The use of composites in the consumer goods industry includes home furnishings (tables, chair, beds), decorative accessories (lamp bases, flower pot, art objects), housewares, outdoor furniture and garden equipment, home power tools, sports equipment, and photographic equipment (camera and projector bodies). Composite use in consumer goods accounts for about six percent of all reinforced plastics and, with the exception of sports equipment, glass fiber reinforcements are used almost exclusively.

● Industrial

Industrial applications include construction, anticorrosion, electrical, and appliance uses. Some of the specific applications are listed below:

Construction - Bath fixtures (tubs, showers, and sinks), patio roofs, fences, garage doors, solar panels, signs, building supplies (cladding panels, doors, frames, pillars, roofs, ridge beams), concrete forms, ladders, materials handling equipment, pipe and tubing, storage buildings, ventilation (ducts, hoods, fans).

Anticorrosion - Chemical equipment, filter housings, fuel tanks, plating tanks, pump housings and impellers, tank cars, utility pole hardware, water mains, well casings, pressure bottles.

Electrical - Panels, switch gear, insulators, outlet boxes, transformer covers and pads, flywheels.

Appliance - Dishwasher parts, computer and typewriter housings, refrigerator cases, air conditioner housings, humidifier components.

As with commercial products most of the industrial composites utilize glass as the reinforcement fiber. As long as there is a significant price differential between glass and the advanced fibers there will be little incentive to replace the glass.

2.2.2 Alternatives

When performance is an overriding factor, "advanced composites have been used in place of glass composites. This has happened in aviation, space, and sporting goods to list a few.

The key phrase of our national space effort from the beginning was "weight reduction." In an effort where it takes 20 pounds of fuel and engine to lift one pound of payload off the ground, weight savings must be a major consideration. Less weight translates directly into bigger payloads, longer range, or reduced fuel requirements. This concern for weight was a major factor in the development of the current miniaturized solid state electronics and a prime moving force in the development of composite materials. Initially, as with other industries, space applications utilized conventional materials and fiberglass reinforced plastics but the need for ever improved weight reductions and performance has given momentum to the development and use of the advanced composites.

Some of the space vehicles and satellite applications include: rocket engine cases, pressure bottles, tanks, launch tube reinforcements, and air ducting. Advanced fibers used include graphite, Kevlar®, and boron, or combinations of fibers to form hybrid composites.

The use of advanced fibers (graphite, Kevlar®, and boron) in sports equipment was the first successful application of these fibers in the commercial sector. The products include tennis rackets, fishing rods, golf clubs, archery equipment, bicycle frames, hang gliders, ski poles, hockey sticks, surfboards, and helmets. The utilization of advanced composites in sports equipment has been successful because of improved performance. Users claim that equipment made using advanced composites is lighter, better balanced, give better "feel" (stiffness, vibration damping), and have improved damage resistance. Because of this improved performance, the

consumer, especially the experienced sportsman, is willing to pay the cost premium for advanced composite equipment. The premium varies somewhat depending on the amount of advanced fiber in the product. A Head tennis racket using boron fiber retails for about \$80 as compared to the identical racket without boron which retails for \$60. The boron racket contains a small amount (less than 0.2 ounce) of boron in the throat of the racket, a high stress area. On the other hand, an all-graphite tennis racket which has graphite fiber throughout the frame retails for up to \$250.

Although the amount of fiber used in an individual item is not high, the volume is such that the sports equipment industry is a significant market for the fiber producers. Production of the boron tennis racket accounted for significant boron sales since 1975. The sporting goods market has, for the past five years, provided the graphite fiber manufacturers with the minimum sales base which the industry needed to survive. Sales have amounted to about 100,000 pounds per year without which advanced composites would be rarer and more expensive than they are now.

There are limited industrial applications where advanced fibers have been applied because of superior performance. One of these is the use of Kevlar® in flywheels used as energy storage devices. Another is the use of Kevlar® in filament wound pressure bottles. Film cassette holders and patient support devices used in conjunction with medical x-ray equipment are another recent application for Kevlar® and graphite. Composites are used because they have low absorption of x-rays. Low x-ray absorption occurs because of the low density of graphite and Kevlar® fibers, as well as the relatively low density of the resin systems used. The advanced composites provide excellent performance in areas where high structural integrity and stiffness are required to avoid deflection. The elementary truss structure as applied to crane booms and aerial ladders is another application of graphite reinforced plastics. The weight of the graphite can be as low as five percent of the weight of a comparable steel truss.

2.2.3 Prices

Prices of reinforcement glass fibers rose eight percent between 1978 and 1979. Prices in 1979 are summarized below:

chopped strands	\$0.58/lb
roving	\$0.61/lb
chopped mat	\$0.75-0.81/lb

Source: Modern Plastics, 1979.

3.0 ENVIRONMENTAL

Glass fibers are relatively inert, nonbiodegradable, and resistant to incineration. The composites are stable and release few fibers to the environment through normal use. The major pathway of introduction of these fibers to the environment is incineration of glass-resin composites; the resins generally burn off completely, and fibers settle, are trapped in smokestack screens, or are released to the atmosphere. Glass composite products disposed of in landfills would probably release few fibers, though no data are available to substantiate this hypothesis.

4.0 TOXICITY

4.1 HUMAN EXPOSURE

4.1.1 General Population

Very few people are non-occupationally exposed to glass fibers through contact with or use of advanced composites. The resin matrices utilized in these composites do not allow fibers to escape.

4.1.2 Occupational Exposure

People may be occupationally exposed to fibrous glass through the manufacture and fabrication of glass fiber reinforced plastics. Corn (1976) sampled airborne glass fibers in a reinforced plastics operation. The diameter and length distributions, important in toxicological considerations, are summarized in Table 4-1.

TABLE 4-1
AIRBORNE FIBER DIAMETER AND LENGTH DISTRIBUTIONS IN A
FIBROUS GLASS REINFORCED PLASTICS OPERATION

<u>Upper class limit, microns</u>		<u>Percent of fibers < upper class limit</u>
<u>Diameter</u>	1.0	<1
	3.5	35
	5.0	50
<u>Length</u>	5.0	0
	2.0	18
	50.0	25

Median diameter = 5.0 microns Median length = 35 microns
Median aspect ration = 7.0

The majority of the dust generated in the fabrication step was polyester resin.

Source: Corn, 1976.

4.2 PATHOLOGY OF GLASS FIBER

The pathological effects of glass fibers have been studied in great depth. The fiber size determines whether or not it can be inhaled and subsequently cleared out of the body. Most studies to date have addressed the relatively large fibers used in the insulation industry. Most of the fibers are too large to be deeply inhaled, although insulation workers' lungs are contaminated with small fibers also. In addition, it is difficult to extrapolate from this industry to the remainder of the glass fiber industry or to the general population, since many health problems arising from the inhalation of glass fibers are related to the concomitant inhalation of organic solvents used as glues. Although fibrous glass morphologically resemble the asbestiform silicates, its biological action potential is considerably less. The one exception to this rule is fine glass fiber. Extremely slender glass fibers are injurious to lung tissue especially if the fibers are relatively long. The combination of glass fiber inhalation exposure with tubular infection or silica exposure, have a potential effect on one another. Fibrous glass, however, does not have the capacity to cause lung cancer or act as a co-carcinogen even with beryllium salts which are themselves highly carcinogenic. G. W. H. Schepers reported that the responses of four species of experimental animals to the prolonged inhalation of two varieties of fiberglass-reinforced polyester plastics indicated that, although not wholly devoid of capacity to provoke tissue changes, fiberglass/polyester behaved generally like comparatively inert substances. In addition, it should be noted that no identified cases of occupational bronchitis have been linked to exposure to glass fibers. Based on this information in the area of use, glass falls in Group 1, materials for which the potential for hazard is extremely low.

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APPENDIX E
POLYESTER

POLYESTER

1.0 INTRODUCTION

Polyester composites are produced via the curing of a polyester resin in the presence of a reinforcing material. The two most common polyester resins used to formulate polyester composites are polybutylene terephthalate (PBT) and polyethylene terephthalate (PET) (Kline, 1978). Additionally, other aromatic polyesters have also been recently introduced to the marketplace but in a very limited sense and their commercial significance is negligible relative to PBT and PET.

Polyester composites can be either thermoplastic or thermoset materials depending on how the resin is polymerized, the presence of copolymers, and other processing parameters. Currently about 80 percent of all polyester composites are of the thermoplastic type (Kline, 1978). Thermoplastic materials consist of long-chained molecules that are unidirectionally oriented. Thus, the shape of the material can be varied by applying heat and shear stresses. Upon cooling, the material becomes dimensionally stable. Thermoset materials consist of long-chained molecules. However, there is cross-linking among the strands and the material maintains its dimensional integrity upon heating and stressing until it either fails or is thermally degraded.

Polyester resin materials can be modified to tailor the material for a specific use. Some of the more important parameters pertinent to material design are thermal stability, dimensional stability, chemical resistance, electrical properties, and tensile and compressive strengths. The last two properties, and to a lesser extent the other properties, are largely dependent on the presence of chemically inert reinforcing materials.

TABLE 1-1.
POLYESTER (PBT) COMPOSITE TRADE NAMES

Celanex J 105	Dereton
Celanex X 203101	Duranex X 917
Celanex 2001	Hostadur B
Celanex 2011SE-O	Hostadur BUP 8600
Celanex 3310SEO	Hostadur BVP 7600 GV2
Celanex 917	Pocan PBT
Crastin S 600	Tenite
Crastin SG 623	Tenite PTMT 6PROA
Crastin SG 625	Tenite 6PRO
Crastin SG 633FR	Valox
Crastin SG 635FR	Valox 310
Crastin SK 603	Valox 310SEO
Crastin SK 605	Valox 420SEO
Crastin SK 613FR	Versel 1100
Crastin SK 615FR	Versel 1200
Crastin SO 655	Vituf 1661
Dereton TAP 10	Vituf 4884
Dereton TGA 50	

Chemical Structure: Polybutyleneterephthalate

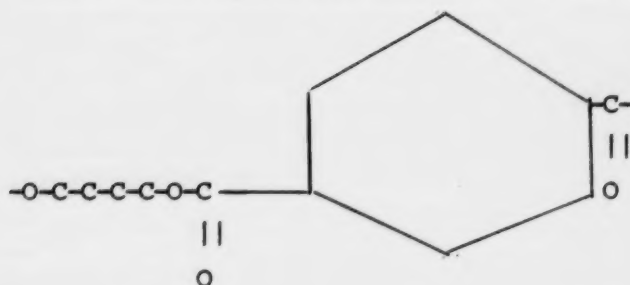
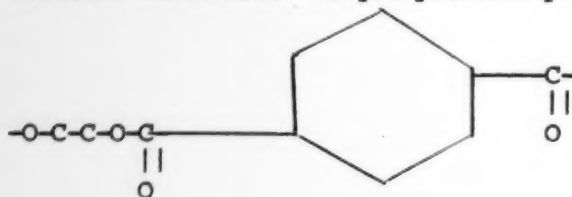


TABLE 1-2.
POLYESTER (PET) COMPOSITE TRADE NAMES

Amilar	KLT 40
Arnite A	Lavsan
Arnite A 04900	Lawsonite (polymer)
Arnite A 200	Lawsonite (VAN)
Arnite FP 800	Lumirror
Arnite G	Lumirror 38S
Arnite G 600	Meliform
Cassappret SR	Melinex
Celanar	Melinex O
Crastin S 330	Mylar
Crastin S 350	Mylar A
Crastin S 440	Mylar C
Daiya Foil	Mylar C-25
Ester	Mylar HS
Estrofol	Mylar T
Estrofol B	Nitron (polyester)
Estrofol Ow	Nitron (VAN)
Fiber V	Nitron Lavsan
Hostadur	Pesoterate
Hostadur A	Scotch Par
Hostadur K	Superfloc
Hostadur K-VP 4022	Terfan
Hostaphan	Tersal (VAN)
Hostaphan RN	Teron
Iambolen	Terphan

Chemical Structure: Polyethyleneterephthalate



2.0 ECONOMIC CONSIDERATION

PRODUCTION AND USE

The domestic production of polyester resins of engineering grades is not reported in the literature but can be inferred from consumption patterns. While the 1979 consumption of all reinforced polyesters was reported to be 868,000 tons, the 1979 consumption of engineering grade PBT and PET thermoplastics was only 27,000 tons (Modern Plastics, 1981). The 1979 and estimated 1980 consumption patterns of engineering grade polyesters are presented in Table 2-1. No data are available pertaining to the import or export of polyester resins although it is unlikely that either is significant for engineering grade material. Table 2-2 illustrates present U.S. capacity to produce polyester resins (SRI, 1980).

The impetus for the development of advanced composites has come primarily from the automotive and aerospace industries where weight savings is critical to fuel savings. Although a typical domestic automobile may contain up to 200 pounds of plastic, only about ten percent of the plastic is fiber reinforced (Davies, 1980). The amount of advanced composites is then, at the most, about 20 pounds per vehicle. In actuality, it is probably less than 20 pounds because not all reinforced plastic can be construed to be advanced composites.

The advanced composites are particularly attractive to the automotive and aerospace industries where the lightweight composite can be substituted for heavier metallic components. Although polyester composites can be used in some aerospace applications, only a small amount is currently used. Epoxy resin composites are the predominant composite material matrices used. In the automotive industry, engineering grade polyesters are used for such items as fan shrouds and other under-hood applications while the truly advanced composites are used for structural applications such as braces and frames. Potential uses include driveshafts, wheels, and high-speed machining parts. Aerospace applications, limited to advanced composites, include stabilizers and high-speed machining parts.

TABLE 2-1.
PATTERN OF CONSUMPTION OF ENGINEERING GRADE PBT/PET

<u>Market</u>	<u>Thousand Tons</u>	
	<u>1979</u>	<u>1980</u>
Appliances	2	2
Electrical/Electronics	9	9
Plumbing and Hardware	3	3
Transportation	10	7
Other	<u>3</u>	<u>2</u>
	27	23

Source: Modern Plastics, January 1981.

TABLE 2-2.
MAJOR UNITED STATES PRODUCERS OF POLYESTER RESINS

			Annual Capacity (Millions of Pounds)
Polybutylene terephthalate resins (PBT resins)			
Celanese Corporation			
Celanese Plastics & Specialties Co., Div.			
Celanese Engineering Resins, Div.	Bishop, Texas	(Celanex®)	70
Eastman Kodak Co.			
Eastman Chem. Products, Ind., subsid.	Kingsport, Tennessee	(Tenite®)	10
Tennessee Eastman Co.	Calvert City, Kentucky	(Gafite®)	10
GAF Corporation	Mount Vernon, Indiana	(Valox®)	130
Chemical Products			
General Electric Company			
Plastics Business Division			
Total			220
Polyethylene terephthalate barrier resins (PET barrier resins)			
American Hoechst Corporation			
Film Division	Greer, South Carolina		75
Hoechst Fibers Indust. Div.	Spartanburg, South Carolina		20
Eastman Kodak Company			
Eastman Chem. Products, Inc., subsid.	Kingsport, Tennessee	(Kodapak®)	55
Tennessee Eastman Co.	Point Pleasant, W. Va.	(Cleartuf®)	240
The Goodyear Tire & Rubber Co.			
Chem. Div.			
Total			390

Source: SRI, 1980.

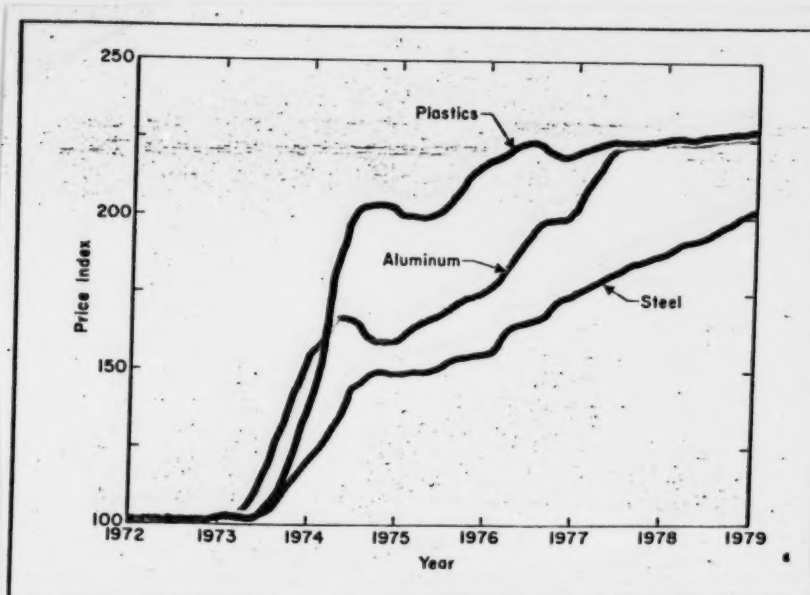
The price of advanced composites presently prevents expansion of their use into markets where their primary asset, lighter weight, is not an important design parameter. In the future, if the cost of the composites becomes competitive with current materials, composites may make inroads into markets currently held by metals and lower grade engineering plastics. The fibers used to make composites account for the bulk of the unit cost. PBT and PET resins are currently priced at \$1.28 and \$.63 per pound, and have not changed significantly since 1979 (Modern Plastics, 1981). Appropriate glass fibers are currently priced at about \$2.50 per pound. Other fibers used to make advanced composites range up to \$110 per pound for some ultra-high modulus graphite fibers (Kaiser, 1978) to \$20 per pound for pitch-based graphite fiber.

FUTURE TRENDS

The growth rate of the manufacture of advanced composites depends on many factors which have a least common denominator -- the profitability of a product using the material relative to the profitability of the same product using conventional materials. The profitability of such a product in turn depends on the material cost, the processing cost, and the degree of marketability enhancement of the product. The relative material cost of plastics versus competing materials from 1972 to date is illustrated in Figure 2-1.

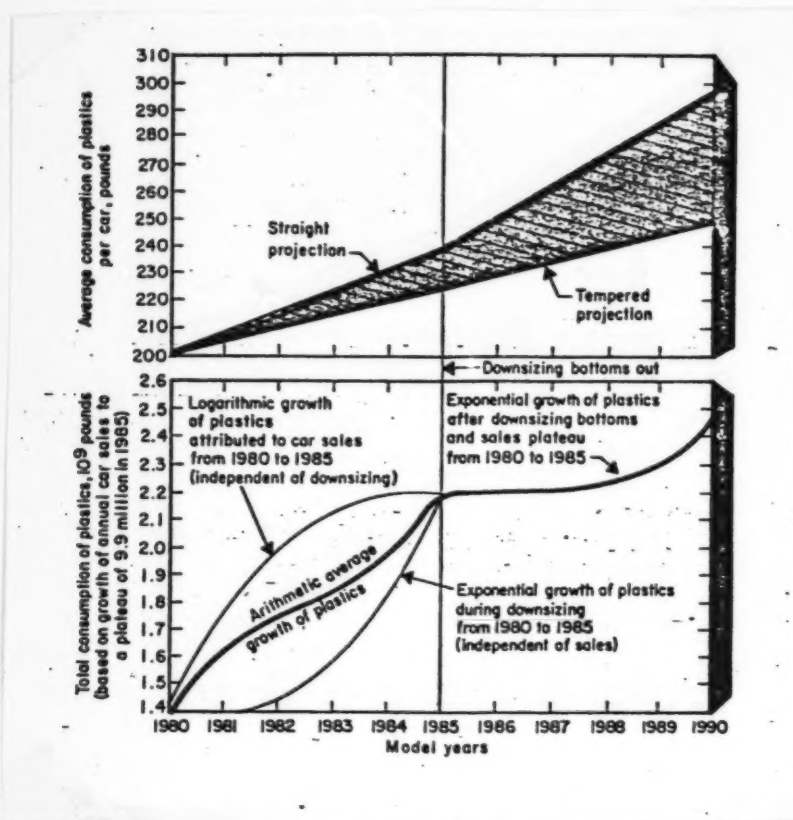
Although plastics are currently competitive with aluminum (a lightweight metal), they are not competitive with steel. Although advanced composites have diverse potential markets, the only market in which the polyester composites are an attractive alternative to metals currently, and in the near future, is the automotive industry where the weight savings enhances the marketability of the product by reducing fuel costs to the consumer. This application of polyesters is not, however, expected to become widespread until after 1985. Automobile producers are currently focusing on downsizing cars to increase fuel efficiency (Davies, 1980; Goldenberg, 1980). Added impediments to the use of composites are the lack of mass-production technology (Modern Plastics, 1979) and the capital costs that would be required to institute this technology. Figure 2-2

illustrates projected trends for the use of plastics in the automotive industry.



The comparative price index, an absolute number here related to a 1972 base of 100, shows that although the costs of plastics, aluminum, and steel have more than doubled since 1973, plastics are now less expensive *relative* to the other two materials. Between 1974 and 1977 this index was higher overall for plastics, but since then the gap between it and aluminum has disappeared, and the gap between plastics and steel has narrowed.

FIGURE 2-1.



Scenario for the growth of plastics in the automotive industry from 1980 to 1990. Graph A (top): The "Straight projection" extrapolates growth in the technically possible area alone, while the "Tempered projection" takes into account such impeding influences as downsizing, low productivity, and limited capital for reinvestment. By 1990, this difference is expected to amount to one-half billion-pounds. Graph B (bottom): From 1980 to 1985: An "Arithmetic" curve is derived by averaging the effects of car sales and downsizing expressed as logarithmic and exponential patterns. Car sales are weighted to have a 50-percent-greater effect than downsizing. From 1985 to 1990: With car sales plateauing and downsizing bottomed out, an extended exponential curve reflects continued and increasing applications of plastics and the evolution of new technologies to the end of the decade.

FIGURE 2-2.

3.0 ENVIRONMENTAL

Few data on the degradation of polyesters or their fate in the environment are available. Thermal degradation kinetics of a dacron polyester were observed at moderate temperatures and seen to follow a standard first order rate of reaction (Papazian, 1972). The results, however, cannot be extrapolated to simulate the incineration of polyester composites.

The resistance of glass-reinforced polyester composites to various chemicals has been evaluated (Theberge, et al., 1971). Table 3-1 presents the results of this research. The glass-reinforced polyester generally performed well under test conditions.

TABLE 3-1.
CHEMICAL RESISTANCE OF GLASS-REINFORCED (30% w/w) THERMOPLASTIC
POLYESTER AT ROOM TEMPERATURE AFTER SEVEN DAYS
INITIAL TENSILE STRENGTH = 19,500 psi

<u>Chemical</u>	<u>Tensile Strength</u>	<u>Grade*</u>	<u>Tensile Strength under 1/4% flexure</u>	
			<u>Strain</u>	<u>Grade*</u>
Hydrochloric acid, 10%	17,860	A	18,450	A
Sulfuric acid, 10%	15,420	F	14,780	F
Acetic acid	18,040	A	17,920	A
Ammonium hydroxide	17,060	F	16,670	F
Heptane	19,680	E	19,810	E
Ethylene glycol	18,040	A	17,470	F
Methanol	18,720	E	17,760	A
Linseed oil	19,080	E	18,410	A
Corn oil	18,290	A	19,130	E
Clorox	18,530	A	18,620	A
Kester #1544 Flux	18,500	A	19,270	E
Lestoil, 2%	16,630	F	15,800	F
Gasoline	17,800	A	17,800	A
Motor oil	18,950	E	19,210	E
Brake fluid	19,680	E	18,780	A

* Grades: E = excellent: 0 to 3% loss of tensile strength
A = acceptable: 3 to 10% loss of tensile strength
F = fair: 10 to 25% loss of tensile strength

Source: Theberge, et al., 1971.

4.0 TOXICITY

Few data on the toxicity of polyesters are available. Two studies of the relative toxicity of polyesters pyrolysis products have been conducted. One study used glass-fiber reinforced polyester with an antimony oxide flame-retardant added. The toxicity of the combustion products to rats was dependent on the temperature used, and deaths were attributed to carbon monoxide poisoning. At 600°C the pyrolysis products of this composite were lethal to eight of the twenty rats, whose blood carbon monoxide levels were 56 percent. The polyester in this test was, however, less toxic than an equal amount of spruce wood (Kimmerle and Prager, 1980).

The relative toxicity of polyester cloth to rats was investigated under varying circumstances. The burn temperature ranged from 200 to 800°C, and air flow ranged from 0 to 48 ml per second. The average time of death of the rats, once exposed, ranged from 5.02 to 9.36 minutes.

No data are available on the toxicity of polyester composites to humans.

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APPENDIX F

EPOXY

EPOXY RESINS

1.0 INTRODUCTION

Epoxies are monomers or prepolymers that react with curing agents to yield high performance thermosetting plastics. Epoxy resins are reinforced with fibers (graphite, glass, Kevlar®, etc.) to form composite materials that exhibit properties such as light weight, toughness, chemical resistance, and superior electrical properties. These epoxy resin composites are used in electrical and structural applications.

The most widely used epoxy resins are the diglycidyl ethers of bisphenol A derived from bisphenol A and epichlorohydrin. Other types are novolac, cycloaliphatic, and hydastoin resins. Conventional resins may range from low viscosity liquids to solid resins. Curing agents commonly used to convert epoxies to thermosets include anhydrides, amines, polyamides, and Lewis acids.

In composite materials, the specific epoxy resin used depends upon the properties (such as high temperature performance) that are required by the manufacturer. For example, high performance resins, such as the tetraglycidyl derivatives of methylenedianiline in combination with draminodiphenyl sulfone is reinforced with graphite fibers to provide a composite material that has good elevated temperature properties and humidity resistance (Kirk-Othmer, 1980).

2.0 ECONOMIC CONSIDERATIONS

PRODUCTION

Most epoxy resins are manufactured from bisphenol A and epichlorohydrin. In addition to bisphenol, other polyols such as aliphatic glycols and novolacs are used to produce specialty resins.

Epichlorohydrin- and Bisphenol A-Derived Resins

Liquid epoxy resins may be synthesized by a two-step reaction of an excess of epichlorohydrin to bisphenol A in the presence of a catalyst. The reaction consists initially in the formation of the dichlorohydrin of bisphenol A and further reaction via dehydrohalogenation of the intermediate product with a stoichiometric quantity of alkali (Kirk-Othmer, 1980).

The use of excess epichlorohydrin minimizes the further reaction of the declycidyl ether of bisphenol A with bisphenol A. The pure diglycidyl ether of bisphenol A is a crystalline solid with a weight per epoxide equal to 170. The typical commercial unmodified liquid resins have a viscosity of 110 to 116 P and an epoxy equivalent weight of approximately 188. Resins of higher molecular weight can be prepared by the taffy process or the advancement process (Kirk-Othmer, 1980).

The taffy process is generally employed for only medium molecular weight resins. The molecular weight of the product is governed by the ratio of epichlorohydrin to bisphenol A. The polymerization reaction results in a highly viscous product (emulsion of water and resin) and the condensation reaction becomes very dependent on agitation. At the completion of the reaction, the water-resin emulsion is separated and the resin is recovered by removing the water under vacuum (Kirk-Othmer, 1980).

Examples of the relationship between mole ratio of epichlorohydrin bisphenol A and the resultant epoxy equivalent of the resin is shown below:

<u>Mole Ratio Epichlorohydrin-Bisphenol A</u>	<u>Epoxy Equivalent Weight</u>
2.6	249
1.57	516
1.33	730
1.2	1,180

Source: Kirk-Othmer, 1980

In the advancement process, liquid epoxy resin is chain-extended with bisphenol A in the presence of a catalyst to yield higher polymerized products. The molecular weight of the resin is a function of the ratio of excess liquid epoxy resin to bisphenol A. The terminal groups are the more reactive epoxy groups. The advancement process is more convenient than the taffy process since higher molecular weight resins can be prepared directly and no by-products are generated (Kirk-Othmer, 1980).

Specialty Resins

In addition to the resins derived from epichlorohydrin and bisphenol A, a variety of other important resins are commercially important. These epoxy resins contain aliphatic, cycloaliphatic, aromatic, and heterocyclic backbones (Kirk-Othmer, 1980).

Glycidylation of active hydrogen-containing structures with epichlorohydrin and epoxidation of olefins with peracetic acid remains the important commercial procedure for introducing the oxirane group into various precursors of epoxy resins (Kirk-Othmer, 1980).

Examples of specialty resins are the epoxy cresol novolac resins, the epoxy phenol novolac resins, bisphenol F resins, polynuclear phenol-glycidyl ether-derived resins, cycloaliphatic epoxy resins, tetraglycidylmethylenedianiline-derived resins, triglycidyl-p-aminophenol derived resins, and hydantoin epoxy resins.

World Production

Worldwide capacity for epoxy resins is estimated at over 440,000 tons. Epoxies are produced in the following countries: Argentina,

Australia, Canada, German Democratic Republic, England, France, Netherlands, India, Japan, Mexico, Spain, Switzerland, and the United States. Over 70 percent of the worldwide production belongs to three American firms - Ciba-Geigy, Dow, and Shell (Kirk-Othmer, 1980). The worldwide use of epoxy resins for advanced composite application is not known but the use in the United States in 1979 was estimated to be 2,000 tons (Lynch, 1980).

United States Production and Major Producers

United States sales of epoxy resins have been steadily increasing since 1971, with the exceptions of decreases during the recessionary years, 1975 and 1980. The use of epoxy resins has doubled during the 1970's and the trend predicted for this resin is for a steady increase of 6 to 8 percent annually (Lynch, 1980). The trend for use of epoxies as composite matrices has fluctuated between 19 and 20 percent annually.

Prices and Trends

The price of epoxy resins have risen rapidly during the past several years as oil prices have escalated. In 1973, epoxy was selling for \$.44 per pound. In 1976, the price jumped to \$.71 per pound and in 1979, the price increased to \$.87 per pound -- double the price in 1973 (Kirk-Othmer, 1980).*

Despite the increase in price the demand for epoxy resins and especially for composites and advanced composites is increasing. Figure 2-1 shows the growth rate for the epoxies during the 1970's.

The use of epoxy resins in advanced composites is expected to increase significantly in the 1980's if better manufacturing methods are found.

* Although the price of epoxy resin has appeared to double since 1973, most of the increase is due to inflation. To eliminate this increase due to inflation, the prices were divided by the consumer price index using 1980 as the base year. Therefore, the prices in 1980 dollars for epoxy in 1973, 1976, and 1979 are \$0.74, \$1.03, and \$0.99, respectively.

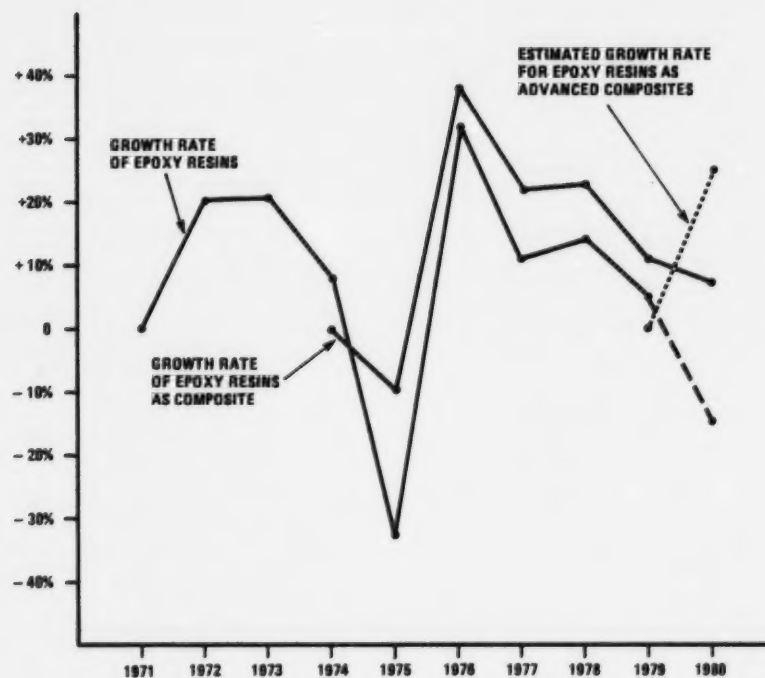


FIGURE 2-1. GROWTH RATE FOR EPOXY RESINS

TABLE 2-1.
TOTAL SALES AND CAPTIVE USE OF EPOXY RESINS AND EPOXY RESINS AS COMPOSITES
IN THE UNITED STATES

Year	Total Sales and Captive Use (millions of pounds)	Fiber Reinforced Laminates and Composites (millions of pounds)	Percent of Total Used As Composite	Advanced Composites (millions of pounds)	Percent of Composites Used as Advanced Composites
1971	151	--	--	--	--
1972	183	--	--	--	--
1973	222	--	--	--	--
1974	240	29	16	--	--
1975	187	26	14	--	--
1976	250	36	14	--	--
1977	278	44	16	--	--
1978	316	54	17	--	--
1979	332	60	18	4	7
1980	316*	64*	20	5-13**	8-20**

* Estimated year end totals

** Approximations made based on projections made by Ciba-Geigy. The advanced composite portion of the market is growing at a rate of 15 to 20 percent per year, but it should plateau and become approximately 8 percent.

Source: Plastics Engineering, December 1980.
Resins, 1980. "How are we doing?"
Frank E. Hall, pp. 18-28.

TABLE 2-2.
MAJOR EPOXY RESIN MANUFACTURERS IN THE UNITED STATES*

<u>Company</u>	<u>Trade Name</u>
Celanese Polymer Specialties	Epi-Rez
Ciba-Geigy	Araldite, Aracast
Dow Chemical	D.E.R.
Reichhold Chemicals	Epotuf
Shell Chemicals	Epon
Union Carbide	Bakelite

Source: Kirk-Othmer, 1980.

CONSUMPTION

Epoxy resins reinforced with graphite, glass, or Kevlar® fibers are principally used in the aerospace and automotive industries. These composites have lightweight and high-strength properties, therefore, they can be used as a substitute for many metal parts. However, high material costs have initially limited the use of these composites. Both aerospace and automotive industries are developing automated manufacturing techniques that promise to be cost effective for high-volume production of these composites.

Aerospace Industry

Epoxy is the major plastic used in aerospace advanced composites. The epoxy is usually used with graphite fibers in a continuous fiber tape or woven-cloth form. The epoxy/graphite advanced composites are characterized by lightweight, high stiffness and high performance properties. The major limiting factors in the application of these composites are two major performance characteristics - temperature and moisture.

Epoxy/graphite composites were once used only for secondary structures and lightly loaded parts in airplanes. Now, they can be used in major wing structures and other critical components. The McDonnell Douglas AV-8B is the first aircraft designed with an all-composite wing. Both main-wing skins and internal parts are constructed of epoxy/graphite, resulting in a light attack aircraft that is 22 percent composites. If this aircraft goes into production, the V/STOL craft would also have the forward fuselage and the horizontal stabilizer constructed of epoxy/graphite composites, thus resulting in an aircraft containing 29 percent composite material (Wehrenberg, 1980).

The Navy's F-18 has over 1,000 pounds of epoxy/graphite in the skin structure, resulting in about 10 percent of the plane's total weight being composites (Wehrenberg, 1980).

Future projections for the use of epoxy/graphite composites is to increase the amount of these composites from 40 to 60 percent of the total

weight in military fighter aircraft. Commercial aircraft (see Figure 2-2) also are using advanced composites in their structural composition, but not to the extent that they are used in the military aircraft. On the 767, 30 percent of the total amount of advanced composites used will be epoxy/graphite cured at 350°F for environmental resistance. The epoxy/graphite composites will be used in the rudder, elevator, aileron, and spoiler applications. The remainder of the advanced composites will be primarily 250°F cure, graphite/Kevlar® hybrids. The total weight saving will be 1,100 pounds.

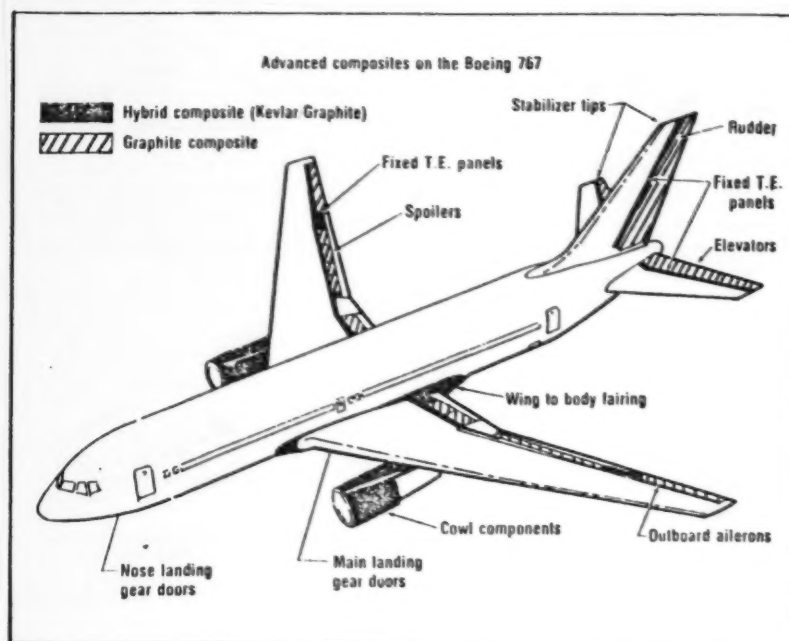


FIGURE 2-2. ADVANCED COMPOSITES ON THE BOEING 767

Source: Wehrenberg, 1980.

Besides graphite, Kevlar®, boron, and glass fibers are also being used as the reinforcements in the epoxy composites. Under NASA Langley's ACEE (Aircraft Energy Efficiency) program, a number of composite structural programs are being studied (Wehrenberg, 1980).

Although epoxy/graphite composites have advantages over metals, there are some drawbacks, such as moisture resistance and heat tolerance, which must be considered. For example, moisture absorption can reduce a 350°F use temperature in an epoxy/graphite system to 250° to 270°F for structural applications. Under ideal conditions, the upper temperature limit for epoxy/graphite is approximately 300° to 350°F. In many of today's aerospace applications, a temperature capability of 600°F would be desirable for use around engines and higher performance missiles (Stedfeld, 1980).

Automotive Industry

The automotive industry is interested in reducing the weight of automobiles in order to improve fuel efficiency.

Epoxy resin advanced composites are not used to a great extent in the automotive industry due to their high price. The epoxy resins are used only in areas that require the epoxy's properties of high stiffness and performance. For example, General Motors Corporation developed an epoxy/glass composite spring to be used as a rear suspension spring in the 1981 Chevrolet Corvette. This spring which weighs eight pounds is lighter and stronger than the replaced ten-leaf steel unit which weighs 41 pounds. GM plans to install composite springs on a large volume car some time in 1981, after which it is expected to become standard on many car lines (Wood, 1980). GM was able to automate the production of this spring making its production competitive with the metal spring that it replaces (Wood, 1980).

Besides, GM, other automotive manufacturers are using the epoxy/graphite composites to reduce the weight of a car, thereby increasing the mileage rating. Ford is experimenting with a car that contains 160 parts made from epoxy/graphite composites. Chrysler is experimenting with the use of epoxy/graphite resins in the driveshaft, leaf spring, etc.

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Projected Uses

The use of epoxy resins in composites is expected to increase significantly if the cost of the fibers and the cost of the production of the composites can be reduced. Advanced composites parts in the aircraft industry have been fabricated by labor-intensive hand operations. Therefore, manufacturers are developing automated manufacturing operations to save on time and labor.

When the costs of epoxy resin composites are reduced, they will be used for more parts in both the aerospace and automotive industries. For example, Ford has developed an experimental car made of an epoxy/graphite composite. The vehicle's body, frame, and chassis parts - 160 parts in all - were made of composite resin. The weight of the car was reduced by 1,250 pounds. Chrysler has evaluated using epoxy/graphite in the manufacture of driveshaft, leaf springs, door hinges, an engine accessory bracket, and valve pushrods (Wehrenberg, 1980).

In the aerospace industry, the epoxy/graphite resins are now being applied to major wing structures and other critical components. New design studies for Air Force fighters show that the next fighter will be in the range of 40 to 60 percent composites. One of the new features being looked at are wing skins made in one big piece of epoxy/graphite. In spacecraft, composites are being evaluated for their use in re-entry vehicles, deployment modules, and fourth stages. For example, one two-piece epoxy/graphite composite part was built as a part of a hardware development program for an advanced ballistic re-entry vehicle that had 21 percent weight saving, passed all test requirements, and indicates a lower production cost (Wehrenberg, 1980).

Possible Alternatives

Manufacturers of epoxy resin composites are developing alternate products that have processing methods that are simpler and have lower costs and that have temperature capability of at least 400 to 450°F.

Modified epoxies such as high-vinyl modified epoxies and vinyl modified bisimide are one approach being evaluated by manufacturers. These

materials have better processing capabilities and are moisture resistant but have limited temperature capabilities (Stedfeld, 1980).

Thermoplastic matrix composites are another possibility being evaluated. Processing of thermoplastics can be done by standard techniques such as layup-and-cure or by matched metal die molding. Thermoplastics such as polysulfone, polycarbonate, polyimides, and polyester are being considered as possible alternatives. Advantages for the thermoplastics composites are cost savings on manufacturing operations, moisture stability, and increased impact resistance over epoxy composites. The major problem with thermoplastic composites is their poor resistance to some commercial solvents, such as ketones and chlorinated hydrocarbons (Stedfeld, 1980).

3.0 ENVIRONMENTAL CONSIDERATIONS

WEATHERING EFFECTS

Epoxy resins themselves have an indefinite shelf life and have little tendency to polymerize spontaneously without curing agents. However, once the resins are cured, they may be subject to environmental effects.

Fiber-reinforced composites, unless they are suitably stabilized and coated, are subject to photoinitiated oxidation which then results in a degradation of the resin surface and eventually a reduction in the composite's mechanical properties. The epoxy-composite resins, however, are not as susceptible to corrosion as many other materials.

Absorbed water is generally not as damaging to the epoxy composite as is sunlight, but its effect may be just as important. There is concern about advanced composites used in advanced aircraft, where absorbed moisture may lower the resin's softening temperature to the point that the material is unable to withstand the severe aerothermal loadings encountered. Cases in which water causes permanent degradation by hydrolysis of chemical bonds is not common. Rainfall in concert with photoinitiated oxidation may produce erosion of the material. The rainfall may then wash away the brittle surface layer so as to expose new material to direct sunlight (Roylance, 1978).

The effects of weathering on advanced epoxy composites are of concern to manufacturers since the physical properties of the composites may deteriorate. Data are not available to evaluate the environmental impact of these effects. However, based on information on weathering effects, the disposal of epoxy resins in landfills is not expected to be a problem. The epoxy resins are expected to remain inert.

DISPOSAL METHODS

Currently, the principal method of disposal of plastic material is landfilling. Data are not available on the leaching of epoxy resins from plastic in a landfill. However, the epoxy resins and advanced epoxy

composite materials are inert, therefore, they are not expected to be a problem in landfills.

The technology to recycle plastics waste is not economical. The cost of recovery, purification, and reformation into a new product of consistent quality does not seem feasible at this time. It is, however, under study by the chemical, automotive, and aerospace industries to try to develop the technology to make recycling feasible. Actual data on the feasibility of recycling epoxy composite materials are not available.

Incineration may also be used to dispose of plastic materials. Data on incineration of the epoxy advanced composite materials are not readily available.

4.0 TOXICITY

Data are not readily available to assess the toxicity of epoxy advanced composites. Only limited data are available on epoxy resins in general.

There is some concern that workers such as those working in automotive repair shops may be exposed to dust from the machining of epoxy resins. A result of inhalation of these dusts may be pulmonary tissue reactions and lung disease (National Bureau of Standards, 1977). Dermatitis may be a problem to workers during the manufacture of the epoxy resins, but dermatitis has not been determined to be a problem to users of epoxy resins.

Epoxy resins have also been evaluated to determine their toxicity due to thermal decomposition. Depending on the method of decomposition (flaming versus pyrolysis), the results ranged from no death or pathological changes for the flaming combustion mode to pulmonary edema, liver and kidney lesions, and death for the pyrolysis products (National Bureau of Standards, 1977).

No data are available to determine toxic effects of epoxy resins and epoxy advanced composites to the consumer under normal exposure conditions. The epoxy resins have been approved by the Food and Drug Administration as liners for food storage. Therefore, the epoxy resins are expected to be inert and not pose a leaching problem into foods (Lynch, 1980).

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APPENDIX C
VINYL ESTER

VINYL ESTER

1.0 INTRODUCTION

Vinyl ester resins, a specialized group of unsaturated polyester resins, are linear reaction products of bisphenol A and epichlorohydrin that are terminated with an unsaturated (vinyllic) acid such as methacrylic acid (Frey and Maffly, 1980; Dow Chemical, 1977; Shell Chemical, 1979). This product is dissolved in styrene solution and is applied and cross-linked in the same way as conventional unsaturated polyesters (Frey and Maffly, 1980). The properties provided by conventional polyester resins such as light weight, adhesion, and creep resistance, are also present in vinyl ester resins. Because of additional properties such as superior strength, superior cure characteristics, added heat, chemical, and solvent resistance, the use of vinyl ester resins may be preferred over conventional polyester resins. Specific properties of vinyl ester resins vary depending upon the specific formulations and their intended uses. A list of pertinent physical properties of those vinyl ester resins identified as being used in advanced composites is presented in Table 1-1.

Vinyl ester resins have chemical stability which is superior to that of conventional polyester resins (Dow Chemical, 1977; Shell Chemical, 1979). Chemical attack on polyester resins in general occurs through hydrolysis of ester groups or the splitting of unreacted carbon-to-carbon double bonds through oxidation or halogenation (Dow Chemical, 1977). The distinguishing characteristic between conventional polyester resins and vinyl ester resins is the position of the double bonds in the two types of polymers (Shell Chemical, 1979; Dow Chemical, 1977). In conventional polyester resins, ester linkages occur randomly throughout the chains, and not all react during polymerization (Shell Chemical, 1979; Dow Chemical, 1977). In vinyl ester resins, the double bonds are at the ends of the molecular chain, react completely on polymerization, and therefore give a more chemically resistant structure (Shell Chemical, 1979; Dow Chemical, 1977).

TABLE 1-1.
PHYSICAL ROOM TEMPERATURE PROPERTIES OF VINYL ETHER RESINS
IDENTIFIED AS BEING PRESENT IN ADVANCED COMPOSITES*

<u>Property</u>	<u>Vinyl Ester Resin</u>			
	<u>Derakane 411</u>	<u>Epocryl 321</u>	<u>Epocryl 322</u>	<u>Epocryl 480</u>
Tensile Strength, psi	11,800	11,600	11,400	12,200
Tensile Modulus, psi x 10	4.9	4.6	4.5	4.7
Elongation, Percent	5	5.0	5.5	5.3
Flexural Strength, psi	18,000	18,600	19,400	17,000
Flexural Modulus, psi x 10	4.5	4.6	4.65	4.70
Compressive Strength, psi	16,600	16,600	16,500	18,900
Compressive Modulus, psi x 10	3.5	3.90	3.80	4.54
Compressive Deformation at yield, percent	6.6	6.7	6.6	8.0
Specific Gravity	1.12	1.12	1.12	1.16
Heat Distortion Temperature, °F	215	210	210	250
Barcol Hardness	35	35	35	35
Monomeric Styrene, Percent	45	50	45	40

* Information presented in this table was obtained from Shell Chemical (1979) and Dow Chemical (1977).

2.0 ECONOMIC FACTORS

PRODUCTION

Manufacturing Process

Manufacturing schemes for vinyl ester terminated polyesters are currently proprietary (Launikitis, 1979).

World Production

The Chemical Economics Handbook (Frey and Maffly, 1980) reported data for world production of unsaturated polyester resins, but no specific data on world production of vinyl ester resins were found.

United States Production and Major Producers

According to the Chemical Economics Handbook (Frey and Maffly, 1980) of the 35 million pounds of high-performance, chemical resistant unsaturated polyester resins produced in the United States on an annual basis, 20 million pounds are of the vinyl ester type involving about 8 million pounds each of bisphenol A and styrene; the balance consists mainly of epichlorohydrin and methacrylic acid. The other 15 million pounds of the high-performance, chemical-resistant resins are estimated by Frey and Maffly (1980) to involve the following approximate quantities of raw materials:

<u>Raw Material</u>	<u>Millions of Pounds</u>
Maleic anhydride	2.5
Chlorendic anhydride	2.3
Isophthalic acid	1
Bisphenol A (propoxylated)	4
Neopentyl glycol	0.7
Other glycols	0.5-0.8
Styrene	4.5

It is noted by Frey and Maffly (1980) that since formulations number into the hundreds and are proprietary, the assumptions reported represent a considerable simplification, and results provide only order-of-magnitude approximations at best. Frey and Maffly (1980) further estimate that of the 105 million pounds of chemical-resistant resins produced in 1979, 21 million pounds were of the vinyl ester variety. The major marketing companies were identified by Frey and Maffly as being Dow Chemical and Shell Chemical Company. The annual capacity of unsaturated polyester resins estimated by SRI as of July 1, 1980, was reported to be 20 million pounds by Dow Chemical under the trade name Derakane and 10 million pounds by Shell Chemical under the trade name Epocryl. Frey and Maffly (1980) note that these estimates are only for condensation capacity dedicated to unsaturated polyester production and may be of limited value. This is evident when comparing the combined estimates of annual capacity in 1980 totaling 30 million pounds for the vinyl ester resins Derakane® and Epocryl® with the 1979 estimated vinyl ester resin production of 21 million pounds.

Prices and Trends

According to industry sources, the price of bisphenol A, chemical-resistant and vinyl ester resins by the truckload was reported to be \$0.97/pound as of May 1980 (Frey and Maffly, 1980). Typical truckload prices are reported by Frey and Maffly to be \$.04 per pound higher than those for bulk quantities. Of the general categories of uses of unsaturated polyester resins, the strongest growth is reported by Frey and Maffly to be in the corrosion resistant sector which includes vinyl ester resins and conventional polyester resins. This sector is reported by Frey and Maffly to suffer the least during the 1980-81 general economic slowdown because the uses are tied to industrial uses rather than residential housing. Shell Chemical (1979) reports that chemically resistant fiberglass reinforced plastics are reported to grow at an annual rate of 18 percent from 175 million pounds in 1976 to 500 million pounds of composites by 1981.

CONSUMPTION

According to Frey and Maffly (1980) the Occupational Safety and Health Administration is likely to restrict the styrene concentration permissible in plants performing open-mold FRP production. A proposed limit of 50 ppm or less is reported by Frey and Maffly (1980) to be widely expected. Such regulations, if implemented, may have detrimental effect on the consumption of resins.

Major and Minor Uses

The major use of vinyl ester resins is in high-performance, chemical-resistant applications where conventional polyester resins are inadequate. Such applications may include chemical process and storage tanks (fuel storage, pickling and plating tanks) fans, blowers, hoods, fume scrubbers, duct systems, and exhaust stacks (Frey and Maffly, 1980). Other applications may include chlorinators, caustic-chlorine cell covers and chlorine headers, air pollution control equipment, filament-wound pipe for water treatment and industrial waste disposal, discharge lines in power plants, structural beams, platforms and grating, ladders, and chemical tanker trailers (Frey and Maffly, 1980). Fertilizer tanks and manure handling equipment are reported by Frey and Maffly (1980) to be examples of agricultural applications.

Projected Uses

In addition to the aforementioned uses, Wehrenberg and Stedfeld (1979) report vinyl esters to be competing with polyesters for use in sheet molding compounds (SMC) as a result of programs to develop high-strength SMC for load-bearing applications. By combining vinyl ester resins and the ITP urethane thickening process Wehrenberg and Stedfeld (1979) quote James Ferrarini of ICI Americas, Inc. as announcing that composites with strengths, impact resistance, and retention of properties and elevated temperatures superior to any system presently available can be made.

Possible Alternatives

No information mentioning alternatives to high-performance, chemical-resistant applications of vinyl ester resins was found. Owens-

Corning Fiberglas reported by Wehrenberg and Stedfeld (1979) to have developed a polyester resin for automotive parts of strength equal to comparable vinyl esters and at lower cost.

3.0 ENVIRONMENTAL

BREAKDOWN

Due to the superior mechanical, heat resistance, and chemical resistance properties of vinyl ester resins, breakdown is not anticipated to occur even under the most extreme environmental conditions. According to Shell Chemical (1979) vinyl ester based systems, even after exposure to corrosive environments for up to two years, often exhibit greater strength properties than the initial values of other resin systems.

The recommended disposal methods for the specific vinyl ester resins identified to be used in advanced composites are controlled burning in an approved incinerator or burial in an approved landfill, in compliance with federal, state, and local requirements for organic material disposal (Dow Chemical, 1979; Shell Chemical, 1979).

4.0 TOXICITY

Vinyl ester resins are solutions of epoxy-based methacrylate esters in styrene monomer. Consequently, the physical hazards of handling vinyl ester resins are mostly those associated with the styrene component (Shell Chemical, 1979; Dow Chemical, 1977). Overexposure to the vapors from this flammable liquid can lead to irritation of the respiratory tract and possibly to anesthesia (Dow Chemical, 1977; Shell Chemical, 1979). Due to the disagreeable odor at relatively low vapor concentrations and the accompanying nasal irritation at concentrations below those necessary to cause systemic effects, willful inhalation of toxic amounts of styrene is unlikely (Dow Chemical, 1977). Toxicological studies on animals have shown that repeated seven-hour exposures to relatively high concentrations of styrene vapors (200 ppm or less) do not cause organic injury (Dow Chemical, 1977). The threshold odor detection of styrene monomer is considered to be in the range of 1 to 10 ppm (Dow Chemical, 1977).

Skin contact with vinyl ester resins for periods of several minutes should cause no irritation (Dow Chemical, 1977). Depending upon the severity of exposure, prolonged contact may cause some irritation and possibly some swelling of the skin (Dow Chemical, 1977). Blistering has been reported to occur when clothing or shoes wet with these materials was worn (Dow Chemical, 1977).

Contact of vinyl ester resins with the eyes may irritate the conjunctival membranes and may cause minor corneal injury (Dow Chemical, 1977).

The acute oral toxicity of vinyl ester resins is low and the chance of ingestion is remote (Dow Chemical, 1977; Shell Chemical, 1979).

No information on toxic effects from use of vinyl ester advanced composites was found. Since there would be no styrene vapors emanating from vinyl ester advanced composites, toxic effects would be expected to be negligible.

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APPENDIX H
FUTURE TRENDS ANALYSIS

FUTURE TRENDS ANALYSIS

In an attempt to refine the mini-assessment that was executed in the body of this report, a "future trends" analysis was performed. The goal of this analysis is to quantify the effects of interaction between significant factors on the future of composite materials.

Specific "events" are postulated and the effect is theorized based on insight gained in developing the mini-assessment. Specific legislation, energy problems, food shortages, inflation, natural resource availability, and population pressure exemplify the type of factors or events that are of interest in a "future trends" analysis. Table 1 presents examples of events in question.

In this "future trends" analysis, the effects of ten events were studied. The resulting analysis is depicted in Table 2 and is briefly described below.

AUTOMOTIVE FUEL PRICES DOUBLE

It was first determined that this "event" is likely to occur by 1990 (90 percent probability) and based on recent history, a 99 percent probability was assigned to this event occurring by the year 2000. This event would greatly accelerate the implementation of composites in automobiles.

AUTOMOBILE DOWNSIZING

The downsizing of automobiles is already taking place. The process is predicted to peak in 1985. After 1985, emphasis will be placed on weight reduction through the substitution of composite materials for metals. Since downsizing actually inhibits the introduction of composites, the effect on composites use is negative.

COMMERCIALIZATION OF THE ELECTRIC CAR

The Electric Hybrid Vehicle 1976 Act will generate new applications for composites. The key to electric vehicle performance is the use of lightweight materials. It is imperative that composites be used in the

TABLE 1
DESCRIPTION OF "EVENT"

Definition

1. Verifiable - occurs at a point in time.
2. Independent - not directly related to historical trends.

Generic Examples

1. Demographic
 - (a) Vital Statistics
 - (1) change in birth rate
 - (2) change in death rate
 - (b) Distribution
 - (1) migration
 - (2) significant shift in age pattern of population
2. Economic
 - (a) Productivity
 - (1) labor productivity increases
 - (2) labor productivity decreases
 - (b) Consumption
 - (1) per capita increase
 - (2) per capita decrease
3. Energy
 - (a) Availability
 - (1) new major source available
 - (2) new type readily available
 - (3) rationed
 - (4) significant price change
4. Technology
 - (a) Breakthroughs
 - (1) fleet mpg improvement
 - (2) genetically modified corn crop
5. Legislation
 - (a) Specifically oriented
 - (1) strict regulation
 - (2) decision to not regulate
 - (3) taxation

TABLE 2
FUTURE TRENDS ANALYSIS

Trend File Name:		Impact (U.S. Composites Production)						
Event No.	Text Describing Important Events	Year/Probability		Years to First Impact	Years to Maximum Impact	Maximum Impact (\$)	Years to Steady State Impact	Steady State Impact (\$)
		1985	1990 2000					
3A	Automotive fuel prices double in real terms (from 1980, \$1.24/gallon no lead regular) (Manufacture of material)	.50	.90 .99	2	5	10	15	20
4A	(Downsizing)	.99	-- --	2	5	--	--	--
5A	Commercialization of Electric Car (EHV 1976 Act)	.20	.50 .70	0	25	2	25	4
4A	Fleet mpg improvement stops at 1980 levels	.20	.20 .20	0	0	0	0	0
3A	Rationing of gas imposed nationwide	.20	.60 .80	2	5	10	15	20
5A	Diesel exhausts proven to be carcinogenic	.20	.20 .20	2	5	1	15	2
3A	Aviation fuel price doubles	.50	.90 .99	5	20	0.01	25	0.02
4A	Manufacturing breakthrough in graphite fiber production costs (\$1/lb)	.10	.50 .60	2	5	5	15	10
4A	Manufacturing breakthrough in composite manufacture rate increase	.30	.80 .90	2	5	10	15	20
5A	Military funding for R&D increased by 100%	.30	.20 .20	5	10	2	20	9

electric vehicle if it is to provide acceptable performance. The steady-state impact is predicted to be only four percent since the fleet size will probably be relatively small.

FLEET MPG IMPROVEMENT STOPS AT 1980 LEVELS

If the fleet mpg improvement is stopped, the incentive to go to composite materials virtually disappears.

NATIONWIDE GAS RATIONING

Gas rationing, like a fuel price increase, will increase consumer demand for increased fleet mpg. Therefore, the implementation of composite materials will be significantly accelerated.

DIESEL EXHAUST PROVEN TO BE CARCINOGENIC

The diesel engine is gaining widespread acceptance in spite of its added cost because of the increased fuel economy it delivers. If the option of going diesel is removed by the fact that it produces a carcinogenic exhaust, the consumer will pay premium prices for vehicles that attain increased mileage by reducing vehicle weight using composites. Therefore, composite use will be positively impacted.

AVIATION FUEL PRICE DOUBLES

The price of aviation fuel has increased dramatically in recent years. This has led the major airlines to demand more fuel efficient aircraft. This also has occurred in general aviation leading to the development of advanced, composite aircraft like the high fuel economy Lear Fan. The increased fuel efficiencies were partially attained by the expanded use of composites. Further aviation fuel price increases would accelerate composite usage in aircraft. Since the amount of composites would ultimately be small because the aviation fleet is relatively small compared to auto fleets, etc., the net increase in composite application would be only about 0.02 percent.

MANUFACTURING BREAKTHROUGHS IN GRAPHITE FIBER PRODUCTION AND MANUFACTURING RATE

A breakthrough in graphite fiber production costs and in manufacturing rates would both lead to greater use of graphite fiber composites. In some cases, this would merely displace glass fiber composites. In others, because of the unique properties of graphite fibers, new applications for composites would be found.

MILITARY FUNDING FOR R&D INCREASED BY 100 PERCENT

Historically, the military has subsidized the development of composite materials. The promise of high performance is the driving force behind this investment. Similar to space program developments, there are significant commercial spinoffs for military R&D efforts. The present price of high performance graphite fibers, about \$20 per pound, is probably a result of military R&D initiated when similar fibers cost over \$400 per pound. Increased military R&D would result in more economically acceptable composite materials.

The above "events" are only "typical" events and are not all inclusive. A much broader analysis would prove valuable in defining the connection between a myriad of "events" and composite materials usage.